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Interlaboratory Evaluation of Measurements for HCN and H2S Released from Wastes

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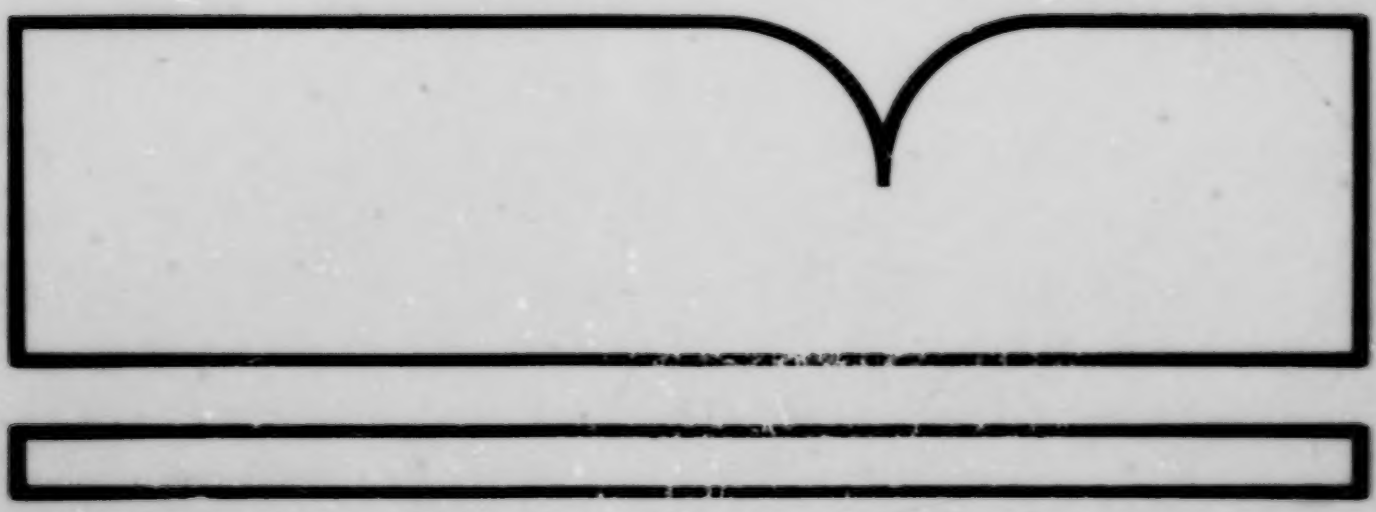

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INTERLABORATORY EVALUATION OF MEASUREMENTS FOR HCN AND H_2S RELEASED FROM WASTES

by

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The objective of this project was to assess a proposed method for determining whether a waste is hazardous on the basis of its release of hydrogen cyanide or hydrogen sulfide upon contact with acidic medium. This was accomplished by performing a single-laboratory evaluation of the method and by conducting an interlaboratory study to estimate method precision. The test method, proposed by the U.S. Environmental Protection Agency's Office of Solid Waste, involves acidifying a waste material to pH 2 and measuring by means of stain tubes the amount of gaseous hydrogen cyanide (HCN) or hydrogen sulfide (H_2S) evolved. This report contains a description of the interlaboratory study and an assessment of the proposed method for measuring HCN and H_2S evolved from waste materials.

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ABSTRACT

The objective of this project was to assess a proposed method for determining whether a waste is hazardous on the basis of its release of hydrogen cyanide or hydrogen sulfide upon contact with acidic medium. This was accomplished by performing a single-laboratory evaluation of the method and by conducting an interlaboratory study to estimate method precision. The test method, proposed by the U.S. Environmental Protection Agency's Office of Solid Waste, involves acidifying a waste material to pH 2 and measuring by means of stain tubes the amount of gaseous hydrogen cyanide (HCN) or hydrogen sulfide (H_2S) evolved. This report contains a description of the interlaboratory study and an assessment of the proposed method for measuring HCN and H_2S evolved from waste materials.

In the interlaboratory study, twelve laboratories analyzed eight cyanide-bearing and eight sulfide-bearing waste samples for the gaseous HCN or H_2S evolved upon acidification. The twelve laboratories performed triplicate analyses of the test samples following a detailed set of instructions. Estimates of within-day and across-day repeatability and reproducibility were determined for the sample measurements.

Based on the interlaboratory results, the proposed method for measuring H_2S evolved from waste materials was shown to be potentially useful. However, the measurements for HCN from waste samples were not reliable because of an interference that produced a stain on the detector tubes. Carbon dioxide can produce an interfering color change on HCN stain tubes, and mass spectrometric measurements confirmed that carbon dioxide was the major gas evolved from the cyanide wastes investigated.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ASTM	-- American Society for Testing and Materials
cm	-- centimeter
EPA	-- U.S. Environmental Protection Agency
g	-- gram
L	-- liter
mL	-- milliliter
N	-- normality
OSW	-- Office of Solid Waste
PE	-- performance evaluation
ppm	-- part per million
QA	-- quality assurance
QC	-- quality control
RCRA	-- Resource Conservation and Recovery Act
% RSD	-- percent relative standard deviation
RTI	-- Research Triangle Institute
Std. Dev.	-- standard deviation
μg	-- microgram
μL	-- microliter

SYMBOLS

A,B,...,H	-- sample code identifiers
CO_2	-- carbon dioxide
HCl	-- hydrogen chloride
HCN	-- hydrogen cyanide
H_2S	-- hydrogen sulfide
H_2SO_4	-- sulfuric acid
K_1,K_2,K_3	-- constants from Appendix B
KCN	-- potassium cyanide
KOH	-- potassium hydroxide
Na_2S	-- sodium sulfide
NH_3	-- ammonia
NO_2	-- nitrogen dioxide
pH	-- logarithm of reciprocal of hydrogen ion concentration
R_ω	-- estimate of repeatability
R_2	-- estimate of reproducibility
S_1	-- standard deviation for repeatability
S_2	-- standard deviation for reproducibility

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SECTION 1

INTRODUCTION

The United States Environmental Protection Agency (EPA) has specified in the Federal Register[1] that a solid waste exhibits the characteristic of reactivity if "it is a cyanide- or sulfide-bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment." At the present time, there are no suitable, validated procedures for determining HCN or H_2S evolved from waste materials.

The objective of this project was to assess a method for determining whether a waste is hazardous on the basis of its release of hydrogen cyanide or hydrogen sulfide upon contact with acidic medium. This was accomplished by performing a single-laboratory evaluation[2] of the test method and by conducting an interlaboratory study to estimate method precision. This report contains a description of the interlaboratory study and an assessment of the proposed method for measuring HCN and H_2S evolved from waste materials.

Under EPA Contract No. 68-03-2961 with the Environmental Monitoring Systems Laboratory in Las Vegas, the EAL Corporation (Richmond, California) has developed a method according to a concept proposed by the EPA Office of Solid Waste (OSW). The procedure (in Appendix A) involves acidifying the waste material to pH 2 and measuring by means of stain tubes the gaseous hydrogen cyanide or hydrogen sulfide evolved. In this method, test solutions are not purged with a carrier gas because this process would not reflect disposal conditions.

Gas detector tubes are available commercially that have been designed to develop stains when exposed to specific gases.[3] The length of the stain developed in a gas detector tube reflects the amount of the specific gas sampled (when no other gas present causes a color change). Stain tubes with calibrated scales are available. Use of stain tubes to detect and measure toxic gases is rapid and requires no special instrumentation or extensive training.

After acidification of the waste sample in the prescribed reaction flask (Appendix A), the evolved gas is pumped through a graduated stain tube (National Draeger, or equivalent). The material in the HCN tube from Draeger (Catalog No. 67-28441) reacts with HCN to form HCl.[3] In the presence of methyl red, the HCl gives a red stain front on a tube scale of 0.0 to 120.0 µL. Although a protective layer collects several acidic and basic interfering gases, high concentrations of NH_3 and NO_2 can produce a yellow and dark orange coloration,

respectively. The Draeger H_2S tube (Catalog No. 67-28141) contains a lead compound which reacts with H_2S to give a brown stain front on a tube scale of 0.0 to 60.0 μL.[3] The major H_2S interferent is reported to be sulfur dioxide.

STUDY OVERVIEW

The interlaboratory study consisted of the analysis of eight sulfide-bearing and eight cyanide-bearing waste samples for evolved H_2S or HCN by the test method (see Appendix A). Twelve laboratories participated in this study. They performed triplicate analyses of the test samples following a detailed set of instructions (see Section 2). In every case, two determinations were carried out on the same day and the third on a different day. In this way, estimates of within-day and across-day repeatability and reproducibility were obtained for sample measurements.

The interlaboratory results were reported on data sheets sent to the Research Triangle Institute, Post Office Box 12194, Research Triangle Park, North Carolina, 27709. The data are presented in this report. The participating laboratories are identified by and referred to by number (01 to 14, excluding 03 and 13). A refined description of the method is provided in Appendix A.

SAMPLE ACQUISITION

Six cyanide-bearing and five sulfide-bearing wastes were collected by the Energy Resources Company, Inc., Cambridge, Massachusetts, and homogenized before use in the interlaboratory study. Sample collection was conducted following the protocol in a publication by the EPA Office of Solid Waste.[4] Eight cyanide test samples were prepared from the six cyanide wastes by including two pairs of duplicates (HCN-D is a duplicate of HCN-G and HCN-E is a duplicate of HCN-H). Eight sulfide test samples were prepared from the five sulfide wastes by including a pair of duplicates (H_2S-D and H_2S-G) plus two spiked liquid samples (H_2S-A and H_2S-B). The waste types are indicated in Table 1.

TABLE 1. SAMPLE DESCRIPTION

Sample No.	Description	Study No.
Cyanide-Bearing Wastes:		
1	Lagoon sludge (electroplating)	HCN-A
2	Filter cake (electroplating)	HCN-B
3	Electroplating sludge	HCN-C
4	Metal hydroxide sludge	HCN-F
5	Fixed metal hydroxide sludge	HCN-D HCN-G
6	Quenching bath residue*	HCN-E HCN-H
Sulfide-Bearing Wastes:		
1	Coal plant wastewater treatment residue*	H_2S-A† H_2S-B†† H_2S-C†††
2	Buffered calcium sulfide waste	H_2S-D H_2S-G
3	Paper mill solid waste	H_2S-E
4	Tannery sludge (N-1)	H_2S-F
5	Tannery sludge (C-2)	H_2S-H

* Samples evaluated during intralaboratory study.

† H_2S-A: Spike (500 mg H_2S/10 mL) added (as Na_2S) to Sample No. 1.

†† H_2S-B: Spike (250 mg H_2S/10 mL) added (as Na_2S) to Sample No. 1.

††† H_2S-C: Sample No. 1 diluted 1:44 with deionized water.

SECTION 2

INFORMATION SENT TO PARTICIPATING LABORATORIES

The reactivity interlaboratory study consisted of the analysis of eight sulfide-bearing waste samples and eight cyanide-bearing waste samples for the gaseous HCN or H_2S evolved using the method developed by EAL (see TEST METHOD below).

TRIPLICATE ANALYSIS

Each waste and performance evaluation (PE) sample was analyzed in triplicate for the evolved HCN or H_2S. The analyte to be determined for each sample was clearly indicated on the sample label. Two of the three measurements were performed on the same day and the third determination on a different day - either before or after the duplicate determination.

ORDER OF ANALYSIS

The analyses of all sulfide solutions and wastes were performed before any cyanide measurements were carried out. See Table 2 for an example of an analysis schedule.

STORAGE

All wastes and standard solutions were refrigerated and protected from light.

ANALYST

The participation of different analysts at the same laboratory was noted. The report form contained space for identifying the analyst by letter (A, B, C, etc.).

REPORTING REQUIREMENTS

The report forms which were filled out by the participating laboratory to transmit analytical results are shown as Tables 3 and 4.

DEADLINE FOR REPORTING RESULTS

The deadline for reporting analytical results was May 23, 1983.

TABLE 2. EXAMPLE OF MEASUREMENT SCHEDULE

The analysis schedule shown below is given for illustrative purposes only. It is not a required schedule of sample measurement.*

Day 1:	H_2S-QC System Check (1)(first ampoule) H_2S-PE1(2); H_2S-A(1); H_2S-B(2) H_2S-C(1); H_2S-D(2); H_2S-E(1)
Day 2:	H_2S-QC System Check (1)(first ampoule) H_2S-F(2); H_2S-G(1); H_2S-H(1) H_2S-B(1); H_2S-A(2); H_2S-PE1(1)
Day 3:	H_2S-QC System Check (1)(second ampoule) H_2S-C(2); H_2S-PE2(2) H_2S-D(1); H_2S-E(2)
Day 4:	H_2S-QC System Check (1)(second ampoule) H_2S-PE2(1); H_2S-F(1) H_2S-G(2); H_2S-H(2)
Day 5:	HCN-QC System Check (1)(first ampoule) HCN-PE1(2); HCN-A(1); HCN-B(2) HCN-C(1); HCN-D(2); HCN-E(1)
Day 6:	HCN-QC System Check (1)(first ampoule) HCN-F(2); HCN-G(1); HCN-H(1) HCN-B(1); HCN-A(2); HCN-PE1(1)
Day 7:	HCN-QC System Check (1)(second ampoule) HCN-C(2); HCN-PE2(2) HCN-D(1); HCN-E(2)
Day 8:	HCN-QC System Check (1)(second ampoule) HCN-PE2(1); HCN-F(1) HCN-G(2); HCN-H(2)

* Numbers in parentheses indicate the number of measurements.

Eight sulfide wastes: H_2S-A to H_2S-H.

Eight cyanide wastes: HCN-A to HCN-H.

TABLE 3. HCN REACTIVITY TASK WORKSHEET

Date: _____

Analyst (denote by letter): _____

Laboratory No.: _____

Sample ID No. (delete lab no.)*					
Sample Wt., g (or mL)					
Water added, mL					
Initial pH					
1N H_2O4 added to pH 2, mL					
Additional H_2SO_4 added, mL					
Pump No.					
Final Pump Flow Rate, mL/min					
Initial Pump Flow Rate, mL/min					
Total gas volume, L					
Tube Reading, µL: 5 min.					
10					
15					
20					
25					
30					
ppm HCN in gas pumped (Tube reading/Total volume)					
HCN evolved, µg (Tube reading x 1.1)					
µg HCN/g sample					

* Include all study data: daily QC system checks, PE samples, and waste samples. For samples which require triplicate measurements, place an ordinal number after sample ID No. (e.g., HCN-B1, HCN-B2, HCN-B3).

TABLE 4. H_2S REACTIVITY TASK WORKSHEET

Date: _____

Analyst (denote by letter): _____

Laboratory No.: _____

Sample ID No. (delete lab no.)*					
Sample Wt., g (or mL)					
Water added, mL					
Initial pH					
1N H_2SO_4 added to pH 2, mL					
Additional H_2SO_4 added, mL					
Pump No.					
Final Pump Flow Rate, mL/min					
Initial Pump Flow Rate, mL/min					
Total gas volume, L					
Tube Reading, µL: 5 min.					
10					
15					
20					
25					
30					
ppm H_2S in gas pumped (Tube reading/Total volume)					
H_2S evolved, µg (Tube reading x 1.4)					
µg g H_2S/g sample					

* Include all study data: daily QC system checks, PE samples, and waste samples. For samples which require triplicate measurements, place an ordinal number after the sample ID No. (e.g., H_2S-B1, H_2S-B2, H_2S-B3).

QUALITY CONTROL SYSTEM CHECKS

At the start of each analysis day, a quality control system check was carried out by measuring the gaseous HCN or H_2S evolved from a reference solution. The solution used contained the analyte being measured that day. These standards were supplied to each laboratory and were prepared and handled as follows:

Two ampoules containing Na_2S and two containing KCN concentrated stock solutions were shipped to each laboratory. The cyanide and sulfide solutions were labelled HCN-QC and H_2S-QC, respectively. After opening the first ampoule of each analyte, the contents were transferred to one of the enclosed vials and placed in a refrigerator.

One half mL of the stock solution (H_2S-QC or HCN-QC) was diluted to 100 mL with H_2O, and 10 mL of the resulting solution was used for the system check. This diluted working standard was prepared each analysis day. The details of the measurement process are described below in the TEST METHOD. Depending on the volume of gas pumped through the system, the stain front for a QC check should read between 1/3 and 2/3 of full scale. The actual tube reading was recorded on the appropriate report form.

Approximately one-half of the total estimated number of 0.5-mL daily aliquots was withdrawn from the first ampoule. The maximum number of 0.5-mL aliquots withdrawn from one vial did not exceed 5, and the vial contents were not used after storage for 1 week. When either of the above conditions had been met, the second QC ampoule was opened, its contents transferred to a second vial, stored in a refrigerator, and used as the source of the 0.5-mL stock solution for the remainder of the study.

PERFORMANCE EVALUATION SAMPLES

Two performance evaluation samples of each analyte were sent to each participating laboratory. These samples were labelled H_2S-PE1, H_2S-PE2, HCN-PE1, and HCN-PE2. Three ampoules of each test solution were provided.

From each of two ampoules, 10 mL of H_2S-PE1 were analyzed for evolved H_2S during the first day of H_2S measurements. In the same manner, 10-mL aliquots of HCN-PE1 from each of two ampoules were analyzed for HCN during the initial HCN measurements. The third ampoule of each PE1 set was opened and its contents analyzed on any other day when waste samples were being analyzed for that gas.

Two ampoules of each PE2 sample set were opened and their contents analyzed after 16 waste measurements had been performed (one sample analyzed in triplicate produced three measurements). The third ampoule from each PE2 set was opened and its contents analyzed on any other day when waste samples were being analyzed for that gas.

SAMPLE CODING AND DISTRIBUTION

Each participating laboratory was assigned a number which was used to code waste and standard samples and to identify individual laboratories in reports. For example, Laboratory No. 02 received the following samples:

Eight Sulfide Samples: 02-H_2S-A
02-H_2S-B to 02-H_2S-H

Eight Cyanide Samples: 02-HCN-A
02-HCN-B to 02-HCN-H

QC System Check Solutions: 02-H_2S-QC (two ampoules)
02-HCN-QC (two ampoules)

PE Samples: 02-H_2S-PE1 (3 ampoules)
02-H_2S-PE2 (3 ampoules)
02-HCN-PE1 (3 ampoules)
02-HCN-PE2 (3 ampoules)

TEST METHOD (Adapted From EAL Description)

Scope and Application

This method is designed to measure only the hydrogen cyanide or hydrogen sulfide evolved at the test conditions and not to reflect the total concentration of these gases, or their precursors, in the sample. Variations in temperature, ionic strength, and total volume of the test solution will affect the amount of gas evolved. The total volume of the solution is kept constant from test to test. Ionic strength is not controlled as it is an inherent property of each waste.

Summary of Method

An aliquot of the waste is acidified to pH 2 in a closed system. The gas generated is swept from the reaction chamber using a pump and passed through a calibrated gas detector tube. The detector tube reading is used to calculate the concentration of gas evolved.

Apparatus

Three-neck, round-bottom flask with 24/40 ground glass joints, 250 mL.

Magnetic stirrer bar with magnetic stirring apparatus.

Addition funnel with pressure equalizing line and 24/40 ground glass joint, 125 mL.

Straight, glass adapter tubes with 24/40 ground glass joint and rubber adapter sleeve, 2 each.

Flexible tubing to make connection from detector tube to pump.

Detector tubes: HCN detector tube with range of 10 to 120 μL (Draeger 67-28441 or equivalent). H_2S detector tube with range 5-60 μL (Draeger 67-28141 or equivalent). Detector tubes will be supplied to each laboratory.

pH meter and pH electrode of sufficient length to reach liquid level (approximately 18 cm).

Pump capable of pulling 60 ± 3 mL per minute (MSA Model C-210 or equivalent).

Bubble meter for calibrating pump.

Stopwatch.

Reagents

Sulfuric acid, H_2SO_4 (1N)

QC system checks, supplied as KCN and Na_2S solutions in ampoules.

PE samples, supplied as KCN and Na_2S solutions in ampoules.

Procedure

Place 10 g (or 10 mL) of the waste to be tested into a beaker. Add approximately 80 mL deionized water and determine the amount of 1N H_2SO_4 required to adjust the pH to 2.0.

Place a second 10-g (or 10-mL) aliquot of the waste into the 250-mL, round-bottom flask. Add deionized water in an amount so that the sum of the volume of water and the volume of 1N H_2SO_4 required for pH adjustment will equal 100 mL. Use the same volume of 1N H_2SO_4 for subsequent measurements of the same sample.

Assemble the apparatus as shown in Figure 1 using the proper detection tube.

Calibrate the pump in line to a flow of 60 ± 3 mL/min using the bubble meter attached to the pump outlet. The flow rate will be recorded before and after the measurement period with the Draeger tube attached to the inlet end of the pump for each analysis.

Begin stirring the test mixture; and make sure all connections are tight.

Carefully adjust the test solution to pH 2.0 using the 1N H_2SO_4.

Note the readings of stain length at 5-minute intervals. If the length of the stain exceeds the capacity of the detector tube, reanalyze the sample using a smaller aliquot. If very little or no stain develops, perform triplicate measurements and report results.

After 30 minutes, stop the pump and record the final detector tube reading.

QC system checks and PE samples are delivered by volume (10 mL).

Calculations

Total air volume = Pump flow rate (final + initial)/2

ppm H_2S or HCN in gas evolved = Tube reading/Total volume

HCN evolved, μg = Tube reading x 1.1

H_2S evolved, μg = Tube reading x 1.4

HCN or H_2S, μg per g sample = μg (HCN or H_2S)/wt. of sample, g

Enter the above data on the report forms for submission to the Research Triangle Institute (RTI), Research Triangle Park, North Carolina.

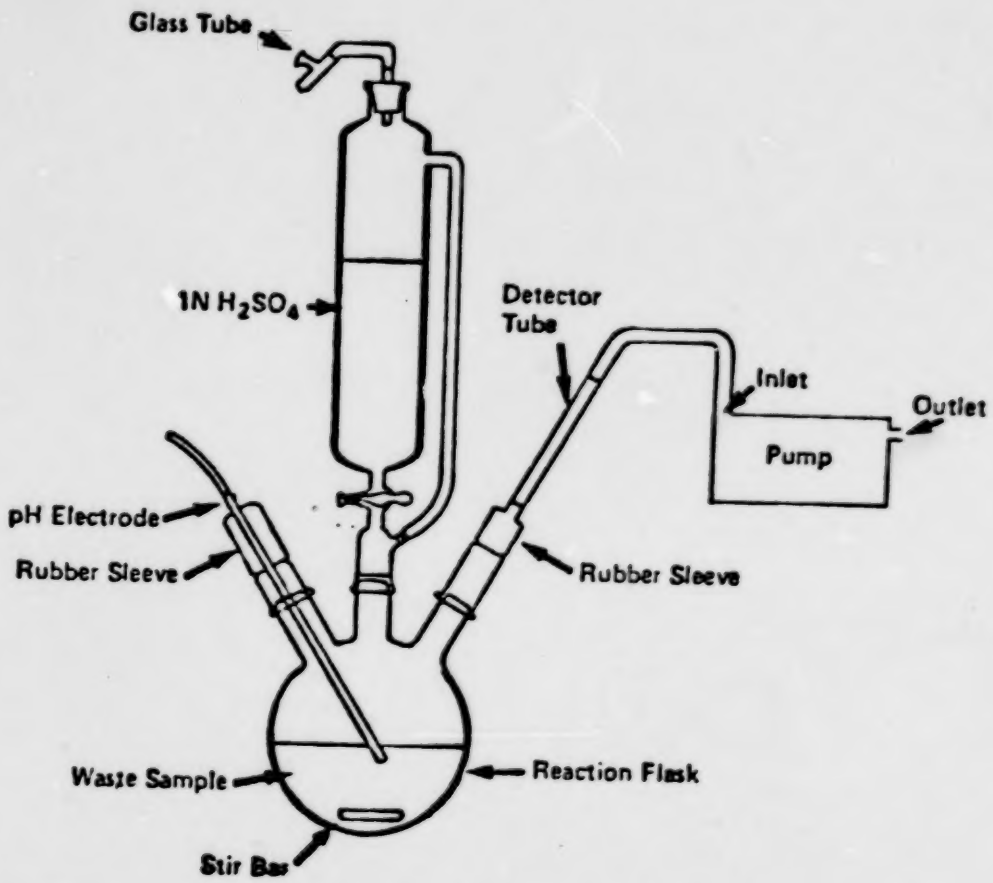

Figure 1. Test apparatus.

SECTION 3

RESULTS FROM COLLABORATIVE STUDY

A complete tabulation of all HCN and H_2S sample results appears in Appendix C and D, respectively. Since samples HCN-C and H_2S-C were reported containing no analyte by all laboratories, no tables were prepared for these samples. Included on each report form is a statistical summary of the standard deviation for repeatability and reproducibility and the estimate and coefficient of repeatability and reproducibility.

The overall precision values for the HCN and H_2S measurements are shown in Tables 5 and 6. The repeatability and reproducibility coefficients for the waste samples were determined according to the procedure in Appendix B and are listed in Tables 7 and 8. In compliance with the recommendations in Standard E 173 of the American Society for Testing and Materials (ASTM)[5], the repeatability coefficient is used here to represent the 95-percent confidence limit for the difference between two determinations by a typical single laboratory expressed as a percent of the average concentration for a sample, and the reproducibility coefficient is used here to represent the 95-percent confidence limit for the difference between two determinations by two typical laboratories (one determination by each) expressed as a percent of the average concentration for the sample. For example, the precision data in Table 7 for sample HCN-D show that the best agreement between duplicate measurements is expected when the tests are run on the same day in a single laboratory (90 percent). Second-best precision for sample HCN-D is expected when the measurements are obtained in a single laboratory but on different days (120 percent, 170 percent). On average for the samples examined in this study, the HCN reproducibility (either within-day or across-days) is approximately twice the repeatability.

TABLE 5. HYDROGEN CYANIDE MEASUREMENT PRECISION

Waste Sample	Measurements	Average Concentration (μg/g)	RSD* (%)
HCN-A**	24	0.26	32
HCN-B	33	5.6	91
HCN-D	32	2.2	100
HCN-E	30	1.4	62
HCN-F	30	0.14	150
HCN-G	31	2.9	130
HCN-H	30	1.3	75

* Relative standard deviation of individual measurements from all laboratories.

** Outlier values from one laboratory have been excluded (see Appendix C).

TABLE 6. HYDROGEN SULFIDE MEASUREMENT PRECISION

Waste Sample	Measurements	Average Concentration (μg/g)	RSD* (%)
H_2S-A	36	0.48	140
H_2S-B	36	2.4	140
H_2S-D	36	415	27
H_2S-E	36	3.8	27
H_2S-F	33	862	64
H_2S-G	35	367	56
H_2S-H**	25	420	47

* Relative standard deviation of individual measurements from all laboratories.

** Outlier values from one laboratory have been excluded (see Appendix D).

TABLE 7. REPEATABILITY AND REPRODUCIBILITY OF HYDROGEN CYANIDE MEASUREMENTS

Waste Sample*	Parameter	Repeatability Coefficient (%)†	Reproducibility Coefficient (%)†
A#	within day	92	120
	across days	79; 64	140; 140
B	within day	130	250
	across days	180; 100	260; 280
D	within day	90	280
	across days	120; 170	320; 320
E	within day	73	220
	across days	81; 140	200; 200
F	within day	230	510
	across days	440; 370	450; 480
G	within day	350	410
	across days	260; 210	370; 330
H	within day	57	250
	across days	85; 110	190; 220
Average**	within day	150	290
	across days	170	280

* Waste sample HCN-C is not included in list because no measurable values were reported.

† See Appendix B for equations.

Outlier values from one laboratory have been excluded (see Appendix C).

** Testing the differences in repeatability and reproducibility (within-day and across-days) by t-Test:

Repeatability - not statistically significant at 5% level.
Reproducibility - not statistically significant at 5% level.

TABLE 8. REPEATABILITY AND REPRODUCIBILITY OF HYDROGEN SULFIDE MEASUREMENTS

Waste Sample*	Parameter	Repeatability Coefficient (%)†	Reproducibility Coefficient (%)†
A	within day	58	460
	across days	340; 280	450; 430
B	within day	20	460
	across days	270; 240	480; 470
D	within day	22	90
	across days	65; 82	71; 81
E	within day	21	57
	across days	86; 76	93; 76
F	within day	78	180
	across days	140; 150	230; 200
G	within day	55	160
	across days	72; 79	190; 220
H#	within day	84	120
	across days	120; 160	110; 150
Average**	within day	48	220
	across days	150	230

* Waste sample H_2S-C is not included in list because no measurable values were reported.

† See Appendix B for equations.

Data pairs containing an outlier value have been excluded (see Appendix D).

** Testing the differences in repeatability and reproducibility (within-day and across-days) by t-Test:

Repeatability - statistically significant at 5% level.
Reproducibility - not statistically significant at 5% level.

SECTION 4

INTERLABORATORY QUALITY ASSURANCE

The results reported for the quality control system checks and the quality assurance performance evaluation samples are summarized in Tables 9 and 10.

In Table 9 it is shown that for HCN the interlaboratory variability (% relative standard deviation) of the mean daily quality control system checks is 17 percent, which coincides with the 17 percent method precision figure reported by EAL (see Appendix A). The quality assurance performance evaluation results gave comparable precision estimates. It is also noteworthy that the recovery in the gas phase for the generated HCN is between 5 and 6 percent, which is in the range reported by EAL and confirmed by RTI. When HCN and H_2S are generated by acidifying salt solutions, recoveries of these compounds as gases are less than 100 percent because of the solubilities of these gases in aqueous media. The much lower recovery for HCN than for H_2S is a reflection of the much larger partition coefficient between liquid and vapor phase for HCN than for H_2S (238 versus 2.76 at 20°C).[6]

Table 10 shows the interlaboratory precision estimates for H_2S quality assurance/quality control samples. The 68 percent recovery in the gas phase for the generated H_2S is in the range reported by EAL and also found in preliminary work at RTI.

The quality assurance and quality control results submitted by the participating laboratories indicate performance consistent with method characteristics reported by EAL and determined independently at RTI.

TABLE 9. HYDROGEN CYANIDE QA/QC RESULTS

Lab No.*	QC System Check Mean Tube Reading, µL	QA Samples Mean Conc., µg/mL PE-1	PE-2
01	31	8.4	2.5
02	25	6.6	3.2
04	28	8.0	2.8
05	23	7.1	2.3
07	24	6.8	2.6
08	22	6.8	2.4
09	32	7.5	2.7
10	22	6.5	2.4
11	33	10.5	3.4
12	**	**	**
14	**	**	**
Mean	26.7	7.6	2.7
Std. Dev.	4.4	1.3	0.38
% RSD	17	17	14
HCN Added	454 µL	150 µg/mL	50 µg/mL
Mean Recovery	5.9%	5.1%	5.4%

* Laboratories 03, 06 and 13 did not report data.

** The PE and QC samples appear to have been interchanged.

TABLE 10. HYDROGEN SULFIDE QA/QC RESULTS

Lab No.*	QC System Check Mean Tube Reading, µL	QA Samples Mean Conc., µg/mL PE-1	PE-2
01	21	0.0	3.8
02	22	0.2	2.2
04	16	0.0	4.1
05	37	0.0	3.0
06	31	0.1	4.5
07	18	0.3	2.2
08	24	0.0	4.3
09	22	0.0	3.9
10	24	0.0	2.8
11	26	0.0	4.4
12	21	1.5	2.4
14	24	1.2	4.4
Mean	23.8	0.06**	3.5
Std. Dev.	5.6	0.06**	0.92
% RSD**	24	100**	26
H_2S Added	37 µL	0.0 µg/mL	5.0 µg/mL
Mean Recovery	66%	-	70%

* Laboratories 03 and 13 did not report data.

** Outlier values from two laboratories have been excluded.

SECTION 5

COMMENTS RECEIVED FROM PARTICIPATING LABORATORIES

The laboratories were requested to comment on any aspect of the test methods which they felt required special mention. Most of the laboratories responded to this request. Their comments are listed below.

LABORATORY 01

Hydrogen Cyanide

In those cases where large amounts of acid were needed to adjust the pH to 2, the tube turned a red-orange color which obscured the HCN red stain front. For example, 10 g of sample HCN-H required 100 mL of 1N H_2SO_4.

If provided with more sample and allowed more time, we could have optimized the amount of sample used in the test to ensure complete gas evolution during the 30-minute collection period and a stain front 1/3 to 2/3 of full scale.

Recommendations--

Factors in test protocol that could be more completely described:

(a) Ventilation required,

(b) Disposal of tested and untested material,

(c) Medical first aid in the event of exposure.

Homogeneity of a sample will influence usefulness of test.

LABORATORY 04

Hydrogen Sulfide

Quality control samples run on the third or fourth day were prepared in dilute caustic that seemed to preserve the sulfide better and allow higher recoveries. Only PE-2 contained sulfide; PE-1 was free of sulfide.

Hydrogen Cyanide

Carbon dioxide produces a pink yellow coloration which clears up after 20 to 25 minutes. The cyanide stain front increases beyond the 30-minute collection period; the front increased from 27 to 36 µL after 45 minutes.

LABORATORY 05

Hydrogen Sulfide

The tubes seemed to be well-suited for this application due to the specificity of the indicator reaction.

Hydrogen Cyanide

The HCN-QC samples gave a stain front which advanced to approximately 1/6 of full scale, not in the ideal 1/3 to 2/3 of full scale region.

In some cases, the red stain front was diffuse and hard to read due to formation of orange- and yellow-colored interferences on tube. This was particularly true for samples HCN-D and HCH-G and led to some indecision in reading tubes. In other cases, an interfering orange color faded before the 30-minute measurement period was over. This occurred during the analysis of samples HCN-A and HCN-B.

In general, the HCN tubes were difficult to use. Stain fronts were less definitive with HCN than with H_2S.

Airflow

Design change suggested so that flow is directed across the entire flask (move addition funnel) or extend addition funnel below sample surface. The latter modification would eliminate the need for stirring the sample after pH adjustment.

Sample Size

Ten grams of certain samples required more than 100 mL of 1N H_2SO_4. Directions are needed for these situations. The need for a set procedure for cases where less than 1 gram of sample is required. Has a study been carried out to show linear relationship between sample weight and amount of H_2S/HCN evolved?

General

Has study been done on effect of stirring rate on amount of gas evolved?

More detailed directions for equipment set up and operations would have been helpful.

Some of the H_2S-PE1 ampoules contained exactly 10 mL making impossible the delivery of a 10-mL aliquot to the measurement system.

LABORATORY 08

Hydrogen Cyanide

After acidification of sample HCN-G, a red-orange color developed immediately in the stain tube. Since HCN standard solutions did not generate this color, HCN content of HCN-G was reported as zero.

General

Some of the PE ampoules were not completely sealed; some ampoules did not contain 10 mL.

LABORATORY 09

Hydrogen Cyanide

The presence of carbonates gave rise to a pink coloration of the stain tube. This interfering color faded and a normal stain front was evident. This behavior was observed with samples HCN-B, D, E, G, and H.

Acidification

In some samples containing high sulfide levels, the 1N H_2SO_4 was too strong for proper adjustment of the pH (due to small sample size, approximately 50 mg). In other cases, samples HCN-E and HCN-H, 10N H_2SO_4 had to be used to keep the final volume at a reasonable level in the flask.

General

Evolution of gases appeared to be dependent upon stirring speed which is impossible to reproduce with the apparatus used.

Using standard materials, sulfide recoveries were 90 percent and cyanide recoveries were 8 percent.

LABORATORY 10

Hydrogen Cyanide

An immediate coloring of the stain tubes occurred when samples HCN-A, B, C, D, E, G, and H were acidified. The interfering color would sometimes persist during the 30-minute measurement period and make an accurate reading of the HCN stain front very difficult to make.

LABORATORY 11

Hydrogen Cyanide

The acidification of samples HCN-A, B, E, G, and H resulted in the stain tubes turning a mottled yellow-pink color that eventually changed to yellow and

finally to the HCN pink color at the inlet port. The dark pink color associated with the quality control and PE samples was not evident.

When 5 grams of sample HCN-G were used, a yellow-pink mottled color developed on the stain tube that did not revert to yellow. The pink stain front was very difficult to read against this background. The mottled color did not appear when only 2 grams of sample were used, but this experiment gave a low HCN reading.

Large amounts of acid were required to adjust samples HCN-E and H to pH 2.

LABORATORY 12

General

Stain tubes are not suitable for quantitative measurement of hydrogen sulfide or hydrogen cyanide. Results are dependent on too many variables.

SECTION 6

INTERFERENCE STUDY

Some investigative work was conducted to minimize or eliminate interferences with the test method.

HYDROGEN CYANIDE

Collaborative-study samples HCN-A, B, and D through H caused some difficulties during the interlaboratory study as evidenced by the comments from the participating laboratories. The remarks indicated a common interferent in all of the samples (see Section 5).

Carbon dioxide is reported[3] to react with the material in the Draeger HCN tubes to give an overall mottled orange-to-pink appearance, which was noted by analysts at nearly all of the laboratories. In the presence of a limited amount of carbon dioxide, the mottled pink color faded to give a normal cyanide stain front. With samples containing a lot of carbonate, there is not only more effervescence during acidification but also an obscuring stain front that remains even after a prolonged gas sampling period. The outlier values cited in Tables 5 and 7 probably reflect the misreading of the interference stains for HCN stains.

An aliquot of Sample E was acidified and (after 10 minutes) a portion of the headspce gas was removed and injected directly into the ion source of a Varian MAT CH-7 Mass Spectrometer. The resulting mass spectrum indicated the presence of a large quantity of carbon dioxide. An attempt to trap all the evolved carbon dioxide from this waste using a CO_2 stain tube placed in front of the hydrogen cyanide tube was not successful because of the large volume of CO_2 released.

Experiments were performed on cyanide Samples B and E to minimize the adverse effect of carbon dioxide. Sample E released larger amounts of carbon dioxide than Sample B. Several changes were made in the mode of acid addition and measurement time period.

The most successful trials involved the partial acidification of the waste material with 1N H_2SO_4 to a pH between 6 and 8. The system was open; no attempt was made to trap the gases released. The addition of 1N H_2SO_4 was carried out slowly over 5 minutes and the neutralized mixture stirred an additional 5 to 10 minutes or until gas evolution had ceased. The detector tube was put in position, the pump turned on, and the acidification continued to pH 2.

Since the coloring of HCN stain tubes by CO_2 appeared to be reversible to some extent, a gas sampling time in excess of the 30-minute period in the test method was investigated. The success of increasing the sampling time by an additional 30 minutes depended upon the amount of carbonate present in the sample. Samples with relatively low amounts of carbonate (e.g., Sample B) benefited most by this extra gas sampling time. In this situation, the diffuse coloration caused by carbon dioxide faded to give a readable hydrogen cyanide stain front. Samples with large quantities of carbonate (e.g., Sample E) did not benefit from this extra gas sampling time. In the case of Sample E, the slow addition of acid to pH 8 was adequate to render the tube readable.

In summary, the information gained from these experiments has resulted in a potentially useful change in the method before hydrogen cyanide measurements are conducted. The proposed modification appears to minimize the adverse effect of carbon dioxide on Draeger hydrogen cyanide tubes and is summarized below:

> Acidify the sample mixture by slowly adding 1N H_2SO_4 to a pH of 8 without the detector tube or pump connected to the system. Stir the mixture until the evolution of gases has ceased before conducting the HCN determination according to the test method. For samples which still give an unreadable stain front, some improvement may be realized by extending the gas sampling time past 30 minutes.

Tests with standard solutions revealed that purging carbon dioxide at pH 6 and 8 caused a possible 25 percent loss of HCN.

HYDROGEN SULFIDE

Two samples (X and Y; not used in the interlaboratory study) were investigated to identify and to reduce or to minimize the effect of an interference which turned the HCN tubes a dark purple color. Samples X and Y were related in that both were generated from the same industrial process and that Y was obtained by treating Sample X in some manner.

Sample X was acidified and an aliquot of the headspace gas was injected directly into the ion source of a Varian MAT CH-7 mass spectrometer. The resulting spectrum indicated major amounts of carbon dioxide and minor amounts of hydrogen sulfide.

Ten mL of Sample X was analyzed for evolved hydrogen cyanide. The Draeger tube turned a black purple color after 7 minutes. A hydrogen sulfide tube was placed in series between the cyanide tube and the flask. A 10 mL aliquot of Sample X exceeded the capacity of the hydrogen sulfide tube (60 µL) and formed a purple discoloration at the base of the cyanide tube. The stain front on the HCN tube was read at 100 µL. Sample Y was treated in the same manner and indicated the presence of a small amount of hydrogen sulfide (<10 µL) and only 10 µL of hydrogen cyanide (no discoloration).

In an effort to minimize the effect of hydrogen sulfide on the hydrogen cyanide measurement, 10 mL of Sample X was treated with 5 mL of 2N cupric chloride and the test carried out normally with both hydrogen cyanide and

hydrogen sulfide tubes in place. This experiment showed no hydrogen sulfide and 10 μL hydrogen cyanide (1.1 μL HCN/mL Sample X) in the detector tubes.

Treatment of sample X material with a cupric chloride solution is effective in eliminating hydrogen sulfide (which has been shown to be an interferent in the measurement of hydrogen cyanide using a Draeger tube).

SECTION 7

CONCLUSIONS

The suitability of this stain-tube procedure for measuring gaseous HCN and H_2S released from waste materials has been investigated, and the following conclusions are presented:

1. Based mainly on the likelihood of CO_2 interference from cyanide wastes, the use of this stain-tube method (in its present form) for measuring HCN evolved from waste materials is not recommended.

2. The partial-acidification purge technique to reduce the effect of carbon dioxide on HCN measurements shows promise, but must be evaluated on a variety of additional wastes.

3. Based mainly on the absence of interferences and the reasonable analytical precision noted in this study, this stain-tube procedure represents a potentially useful technique for measuring H_2S evolved from waste materials. Optimizing certain test parameters (stirring, acidification, gas sampling time) could improve the precision of the H_2S measurements.

SECTION 8

RECOMMENDATIONS

1. When CO_2 interference is encountered in HCN measurements, one could acidify another portion of the sample to a pH of 8 and stir the mixture (in a hood) until the evolution of gas has ceased before conducting the analysis according to the test method. However, some HCN, together with the CO_2, will be evolved by this procedure. For samples which still give an unreadable stain front, some improvement may be realized by extending the gas sampling time past 30 minutes.

2. Future work should include an investigation of the advantages and disadvantages of performing the CO_2 purge for cyanide wastes at various pH levels with the pump on (but without the HCN detector tube in place). Loss of HCN during any CO_2-purge procedure should be evaluated.

3. Carbon dioxide interference with HCN measurements might prove avoidable by trapping water before it reaches the stain tube (to prevent carbonic acid formation) or by developing an HCN detector tube that involves a different stain reaction.

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APPENDIX A

TEST METHOD TO DETERMINE HYDROGEN CYANIDE AND HYDROGEN SULFIDE RELEASED FROM WASTES

TEST METHOD TO DETERMINE HYDROGEN CYANIDE AND HYDROGEN SULFIDE RELEASED FROM WASTES

1. Scope and Application

1.1 This method is applicable to water, wastewater, and industrial wastes.

1.2 This method provides a fast and simple method to determine if a waste is a reactive waste as a result of its tendency to release toxic levels of hydrogen cyanide or hydrogen sulfide upon contact with an acidic medium. The approach is based on a reasonable "worst case" disposal scenario.

1.3 This method is designed to measure only the hydrogen cyanide and/or hydrogen sulfide gas evolved under the test conditions and not to reflect the total concentration of these gases, or their precursors, in the sample. Variations in temperature, ionic strength, and total volume of the test solution will affect the amount of gas evolved. The total volume of solution is kept constant from test to test. Ionic strength is not controlled as it is an inherent property of each waste. In this method, test solutions are not purged with a gas because this would not reflect disposal conditions.

2. Summary of Method

2.1 An aliquot of the waste is acidified to pH 2 in a closed system. The gas generated is swept from the reaction chamber using a pump and passed through a calibrated gas detector tube. The detector tube reading is used to calculate the amount of toxic gas evolved per gram (or mL) of waste.

3. Sample Handling and Preservation

3.1 Samples containing, or suspected of containing, sulfide or a combination of sulfide and cyanide should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should be commenced as soon as possible, and samples should be kept in a cool, dark place until the analysis is started.

3.2 Samples suspected of containing cyanide wastes, without the presence of sulfide compounds, can be preserved if analysis cannot begin immediately. Samples are preserved by adjusting them to pH 12 with strong sodium hydroxide solution and storing them in a cool, dark place.

3.3 Determinations should be performed in a well-ventilated hood.

4. Interferences

4.1 The analyst should consult manufacturers' literature on the type and nature of potential interferences when using specific detector tubes.

5. Apparatus

5.1 Three-neck, round-bottom flask with 24/40 ground-glass joints, 250-mL.

5.2 Magnetic stirrer bar with magnetic stirring apparatus.

5.3 Separatory funnel with pressure-equilizing tube and 24/40 ground-glass joint, 125-mL.

5.4 Straight, glass adapter tubes with 24/40 ground-glass joint and rubber adapter sleeve, 2 each.

5.5 Flexible tubing to make connection from detector tube to pump.

5.6 Detector tubes: HCN detector tubes with range from 10 to 120 µL (Draeger 67-28441 or equivalent). H_2S detector tubes with range from 5 to 60 µL (Draeger 67-28141 or equivalent).

5.7 pH meter and pH electrode of sufficient length to reach liquid level (approximately 18 cm).

5.8 Pump capable of pulling 60 ± 3 mL per minute (MSA Corporation Model C-210 or equivalent).

5.9 Bubble meter for calibrating pump.

5.10 Stopwatch.

6. Reagents

6.1 Sulfuric acid, H_2SO_4, 1N.

6.2 Cyanide reference solution: Dissolve approximately 2.5 g KOH and 2.51 g KCN in 1 liter of distilled water. Cyanide concentration in this solution is 1 mg/mL.

6.3 Sulfide reference solution: Prepare the solution from crystals of sodium sulfide as described in Method 376.2 (Sulfide, Colorimetric, Methylene Blue) Section 5.8 of "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March, 1979. The solution may be standardized by the titrimetric iodine Method 376.1 of the same publication, although this is not required.

7. System Check

7.1 The operation of the system can be checked using the cyanide or sulfide reference solutions. It is difficult to predict a detector tube reading from a known amount of reference solution due to variations in response of detector tubes of different sources. Reaction flask temperature variations and total volume differences also influence the amount of gases evolved. However, the reference solutions can be used to verify system operation. Replicates can be expected to agree to within approximately $\pm$ 20 percent.

8. Procedure

8.1 Place 10 g (or 10 mL) of the material to be analyzed into a beaker. In a well-ventilated hood, add approximately 80 mL of deionized water and determine the amount of 1N H_2SO_4 required to adjust the solution pH to 2.0.

8.2 Place a second 10-g (or 10-mL) aliquot of the waste into the 250-mL round-bottom flask. Add deionized water in an amount so that the sum of the volume of water and the volume of 1N H_2SO_4, required for pH adjustment, will equal 100 mL.

8.3 Assemble the apparatus as shown in Figure 1 using the proper detection tube or tubes.

8.4 Calibrate the pump in line to a flow of 60 $\pm$ 3 mL/min using the bubble meter attached to the pump outlet. Measure the flow before and after the test period.

8.5 After ensuring that all connections to the apparatus are tight, begin stirring the sample.

8.6 Carefully adjust the test solution to pH 2.0 using the 1N H_2SO_4.

8.7 Record the stain lengths at 5-minute intervals. If the length of the stain exceeds the capacity of the detector tube, reanalyze the sample using a smaller aliquot. If very little or no stain develops, the aliquot size may be increased, depending on the

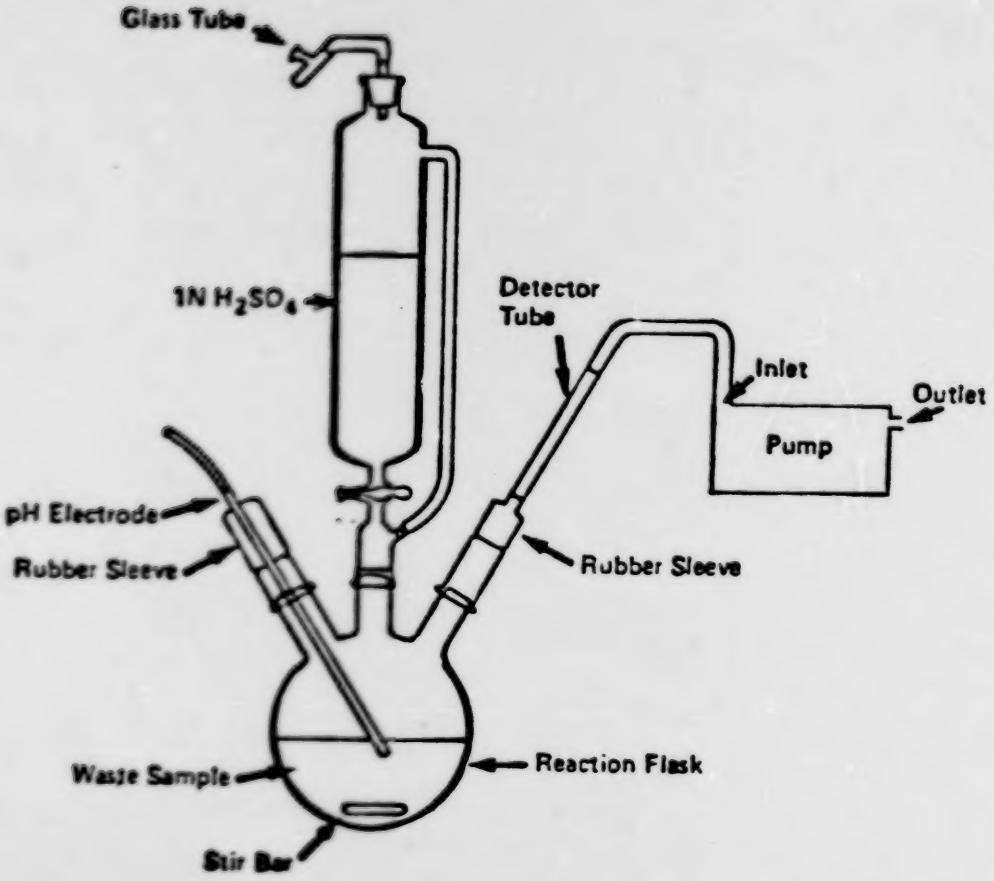

Figure 1. Test apparatus.

nature of the sample. Solid samples require a certain amount of dilution to reach a slurry state so that the acid may contact all portions of the sample and so that efficient stirring may take place.

8.8 After 30 minutes, stop the pump and record the final detector tube reading.

Note 1: The chemistry of some detector tubes may permit their use in series to determine both H_2S and HCN concurrently. When tests were conducted (by the EAL Corporation) with Draeger detector tubes, the H_2S tube had to be placed in front of the HCN tube for satisfactory results. Detector tubes from other manufacturers may perform differently.

Note 2: As an optional step (to determine a "total" evolvable gas value) at the end of the 30-minute test, the pH can be lowered to less than pH 1 and a sand bath used to elevate the temperature. Increased evolution rates may be observed from some samples.

9. Calculations

9.1 HCN evolved (μg) = Stain tube reading (μL) x 1.1 mg/μL*
H_2S evolved (μg) = Stain tube reading (μL) x 1.4 mg/μL*

HCN or H_2S evolved (μg) per unit of sample (g or mL)
= HCN or H_2S (μg)/sample aliquot (g or mL)

Total gas volume (in liters) pumped through stain tube

$$= \frac{(F_1 + F_2)/2 \times T}{1000 \text{ mL/L}}$$

where

F_1 = Pump flow rate (mL/minute) before the analysis
F_2 = Pump flow rate (mL/minute) after the analysis
T = Time duration of pumping (minutes)

9.2 The time of maximum gas evolution rate for a sample can be determined by relating the largest measurement change between 5-minute periods to the elapsed time.

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* Derived from 22.4 liters/mole (at 0°C and an atmospheric pressure of 76 cm of mercury) adjusted to 24.0 liters/mole for laboratory temperatures at 20 ± 10°C. Since gas volume varies with temperature and atmospheric pressure, the gas detector tubes should be graduated in units of mass rather than in volume units.

10. Precision and Accuracy

10.1 Relative standard deviations for the method were found by an interlaboratory study to be 17 percent for HCN (at the 27-µL level) and 24 percent for H_2S (at the 24-µL level).

10.2 The accuracy of the method cannot be determined directly due to the difficulty of providing a sample of known gas evolution qualities. Calibration of the detector tubes used in this method (see Section 5.6) with standard gas mixtures indicate the bias of the H_2S tubes to be approximately 16 percent positive at 20°C and the bias of the HCN tubes to be approximately 35 percent positive at 20°C in an evaluation by the EAL Corporation.

APPENDIX B

ASTM STANDARD E173

Designation: E 173 – 68 (Reapproved 1974)ε

Standard Recommended Practices for CONDUCTING INTERLABORATORY STUDIES OF METHODS FOR CHEMICAL ANALYSIS OF METALS[1]

This Standard is issued under the fixed designation E 173; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

ε NOTE—The second equation in 7.1.2 was corrected editorially in November 1974.

1. Scope

1.1 These recommended practices are intended as a guide to sample distribution and interlaboratory testing to determine the repeatability and reproducibility of methods for the chemical analysis of metals (Note 1). These practices are recommended for use with those methods of analysis of metals that fall under the scope of Committee E-3 providing the prerequisites of these practices are complied with.

NOTE 1—The data required from each laboratory are held to a minimum. This should stimulate the participation of an adequate number of laboratories to provide a valid measure of repeatability and a meaningful evaluation of reproducibility. In view of the referee nature of ASTM methods, the importance of assessing their reproducibility cannot be overemphasized. Therefore, it is recommended that at least ten laboratories take part in the evaluation of each method. Furthermore, it is reasonable to expect any participating analysts who do not have a working knowledge of the method to gain experience with it before applying it to the samples provided for the interlaboratory program.

2. Summary of Method

2.1 Both graphical[2,3] and numerical[4] methods are used for analyzing the data. The graphical presentation of the data permits visual detection of biases, and while it can be used to gain a quantitative measure of repeatability and reproducibility, the numerical method is recommended for the latter use.

3. Definitions

3.1 *repeatability*—a quantitative measure of the variability of the results by a single analyst in a given laboratory, using a given apparatus. It is defined as the greatest difference between two independent results that is to be expected due to random errors on the basis of the 95% confidence level.

3.2 *reproducibility*—a quantitative measure of the variability associated with different analysts and equipment in different laboratories. It is defined as the greatest difference between a result obtained in one laboratory and one obtained in another laboratory that is to be expected due to random errors on the basis of the 95% confidence level.

3.3 *bias*—a systematic error, in contrast to a random error.

4. General Requirements

4.1 *Number of Participating Laboratories*—It is recommended that at least ten laboratories participate in the program; the minimum requirement is five laboratories and eight pairs of values if that statistical method is to be applied. The deficiency in pairs of values resulting from participation by fewer than eight laboratories may be overcome by having

[1] These recommended practices are under the jurisdiction of ASTM Committee E-3 on Chemical Analysis of Metals and are the direct responsibility of Subcommittee E 03.02 on General Analytical Methods.

Current edition approved Sept. 13, 1968. Originally published as E 173 – 60 T. Last previous edition E 173 – 67 T.

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each of a sufficient number submit an extra pair of values. When this is done the second set of duplicate analyses must be made by another analyst, and, if possible, he should use an apparatus different from the one used by the first analyst. In any event he must prepare a second set of standard solutions, perform independent standardizations, calibrations, etc.

4.2 *Number of Samples*—A minimum of two samples of each type of metal or alloy is required, one near each extreme of the concentration range intended to be covered by the test method. Additional samples, evenly spaced throughout the range, are desirable.

5. Specific Requirements

5.1 *Laboratory Samples*—Withdraw enough portions from the gross sample, known to be adequately homogeneous so that one portion may be sent to each participating laboratory.

5.2 *Laboratory Analyses*—Have each laboratory analyze each sample once on each of two days, using the same apparatus both times. Label the result of the first analysis X and the result of the second analysis Y. One analyst must perform both analyses.

6. Graphical Treatment of the Data

6.1 *Construction*—Plot the analytical results from all the cooperating laboratories on rectangular coordinate paper using as large a scale as possible and the same scale on both axes. Let the two values (X and Y) from each laboratory be the coordinates of a single point, appropriately identified as to source. Draw two median lines, one parallel to each axis, such that half of the plotted points (laboratories) lies on either side of each line. If one or two of the points are judged to be definitely separated from the others on the graph, they should not be considered when locating the median lines nor when calculating the precision as directed in Section 7. Draw a third line through the intersection of the median lines so that it forms 45-deg angles with them and has a positive slope.

6.2 *Interpretation*—Characteristics of the method, as written (and presumably as followed), are indicated by the distribution of points on the graph:

NOTE 2—For a more thorough explanation of the interpretation of these graphs, see the previously referenced papers by W. J. Youden.

6.2.1 A long, narrow elliptical distribution indicates a need for modification of the procedure.

6.2.2 Points far from the 45-deg line indicate the need for an investigation within the laboratory involved.

6.2.3 Points on or close to the 45-deg line, but far from the intersection of the lines, indicate some kind of between-laboratory bias.

7. Mathematical Treatment of the Data-Numerical Method

7.1 *Method of Calculation:*

7.1.1 Let X_i and Y_i (i = 1, to n), respectively, denote the first and second test results on two portions of a specific sample analyzed by each of the n analysts; let $\bar{X}$ and $\bar{Y}$ denote the arithmetic averages of the n values of X and Y, respectively; and let K_1 be a constant whose value is a function of n. [$K_1 = 0.886\sqrt{n/(n-1)}$]. To obtain the standard deviation for repeatability (S_1), first compute:

$$D_1 = (1/n)\,\Sigma_{i=1}^{i=n}\,|(X_i - Y_i) - (\bar{X} - \bar{Y})|$$

(Observe that D_1 is the arithmetic average of the values in Column 5 of Table 1, 7.2. The $(\bar{X} - \bar{Y})$ term in this formula is included because it is believed that changes in atmospheric conditions could cause a systematic difference in the X and Y test results.)

Then compute the standard deviation for repeatability:

$$S_1 = D_1 \times K_1$$

and R_1, the estimate of repeatability:

$$R_1 = S_1 \times K_2$$

(Values of K_1 and K_2 corresponding to values of n from 8 to 20 are listed in Table 2.)

7.1.2 To obtain the standard deviation for reproducibility (S_2), first compute

$$D_2 = 1/n\,\Sigma_{i=1}^{i=n}(X_i + Y_i) - (\bar{X} - \bar{Y})$$

(Observe that D_2 is the arithmetic average of the values in Column 7 of Table 1.)

Then compute the standard deviation for reproducibility:

$$S_2 = \sqrt{(D_1^2 + D_2^2)/2} \times K_3$$

and R_2, the estimate of reproducibility:

$$R_2 = S_2 \times K_3$$

(Values of K_3 corresponding to values of n

from 8 to 20 and to values of D_1/D_2 from 0 to 1 are listed in Table 3.)

7.2 *Example of Calculation*—For convenience in making the calculation of repeatability and reproducibility, prepare a 7-column table in which to record the data. In Column 1, record i, the number that identifies the given cooperating laboratory; in Columns 2 and 3, record the determined values, X_i and Y_i, reported by these laboratories; in Column 4, record the corresponding values of $(X_i - Y_i)$; in Column 5, record the absolute values of the quantity $[(X_i - Y_i) - (\bar{X} - \bar{Y})]$; in Column 6, record $(X_i + Y_i)$; and in Column 7, record the absolute values of $[(X_i + Y_i) - (\bar{X} + \bar{Y})]$. Calculate the arithmetic averages of the values recorded in Columns 2, 3, 5, and 7, and designate the average for Column 5 as D_1, and for Column 7 as D_2. An example is given in Table 1.

Calculate R_1, the estimate of repeatability:

$$R_1 = D_1 \times K_1 \times K_2 = 0.0048 \times 0.934 \times 3.14 = 0.014\% \text{ Si}$$

(The values of K_1 and K_2 are taken from Table 2.)

Calculate R_2, the estimate of reproducibility:

$$R_2 = \sqrt{(D_1^2 + D_2^2)/2} \times K_1 \times K_2$$

$$= \sqrt{[(4.8 \times 10^{-3})^2 + (7.8 \times 10^{-3})^2]/2} \times 0.934 \times 3.00 = 0.018\% \text{ Si}$$

(The value of K_2 (for $n = 10$ and $D_1/D_2 = 0.0048/0.0078 = 0.62$) is found in Table 3.)

7.3 *Reporting Precision of Method*—Every method shall contain a statement of precision and shall indicate the number of laboratories that participated in producing the precision data. Treatment of the analytical data as directed in 7.1 and 7.2 leads to values for the estimate of repeatability and of reproducibility (R_1 and R_2) in terms of absolute percent of the element of interest. If similar test programs on other samples at different concentration levels yield essentially constant values for repeatability and reproducibility, the best way to express the precision of the method is simply as absolute percent of the element determined, that is, as R_1 and R_2. On the other hand, if R_1 and R_2 vary with the concentration level, it is appropriate to show more than one value, and if the variability is found to be approximately proportional to the concentration, the precision can be conveniently expressed as the "coefficient of variation," that is, as a percentage of the concentration. In the example given in 7.2, the calculation is as follows:

Coefficient of repeatability = $(0.014/0.2995) \times 100 = 4.7\%$

and

Coefficient of reproducibility = $(0.018/0.2995) \times 100 = 6.0\%$

If fewer than five laboratories can be found to provide the minimum of eight pairs of analytical results, some other expression of precision should be found; a listing of whatever analytical results are available is suggested.

TABLE 1 NBS 20 F (0.299% Si)

i	X_i	Y_i	$(X_i - Y_i)$	$(X_i - Y_i) - (\bar{X} - \bar{Y})$	$(X_i + Y_i)$	$(X_i + Y_i) - (\bar{X} + \bar{Y})$
1	0.298	0.295	+0.003	0.004	0.593	0.006
2	0.302	0.298	+0.004	0.005	0.600	0.001
3	0.298	0.305	0.007	0.006	0.603	0.004
4	0.306	0.302	+0.004	0.005	0.608	0.009
5	0.306	0.309	0.003	0.002	0.615	0.016
6	0.290	0.290	0.000	0.001	0.580	0.019
7	0.294	0.306	0.012	0.011	0.600	0.001
8	0.290	0.300	0.010	0.009	0.590	0.009
9	0.299	0.295	+0.004	0.005	0.594	0.005
10	0.303	0.304	0.001	0.000	0.607	0.008
Avg	0.299 = $\bar{X}$	0.300 = $\bar{Y}$	...	0.0048 = D_1	...	0.0078 = D_2

TABLE 2 A_1 and A_2 Values

Number of Pairs of Values	K_1	K_2
8	0.947	3.26
9	0.940	3.20
10	0.934	3.14
11	0.929	3.11
12	0.925	3.08
13	0.922	3.05
14	0.920	3.03
15	0.917	3.01
16	0.915	2.99
17	0.913	2.97
18	0.912	2.96
19	0.910	2.95
20	0.909	2.94

TABLE 3 A_2 Values

n / D_2/D_1	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	≥1.00
8	3.25	3.24	3.22	3.18	3.13	3.10	3.07	3.04	3.02	3.01	3.01
9	3.20	3.19	3.16	3.13	3.10	3.06	3.03	3.01	2.99	2.98	2.98
10	3.14	3.13	3.12	3.09	3.06	3.03	3.00	2.98	2.97	2.96	2.95
11	3.11	3.10	3.09	3.06	3.03	3.00	2.98	2.96	2.94	2.94	2.93
12	3.08	3.07	3.05	3.03	3.00	2.98	2.95	2.94	2.93	2.92	2.92
13	3.05	3.05	3.03	3.01	2.99	2.96	2.94	2.93	2.92	2.91	2.91
14	3.03	3.02	3.01	2.99	2.97	2.94	2.93	2.91	2.91	2.90	2.90
15	3.01	3.01	2.99	2.97	2.95	2.93	2.92	2.90	2.89	2.89	2.89
16	2.99	2.99	2.97	2.96	2.94	2.92	2.91	2.89	2.88	2.88	2.88
17	2.97	2.97	2.96	2.95	2.93	2.91	2.90	2.88	2.87	2.87	2.87
18	2.96	2.96	2.95	2.94	2.92	2.90	2.89	2.88	2.87	2.87	2.87
19	2.95	2.95	2.94	2.93	2.91	2.89	2.88	2.87	2.87	2.86	2.86
20	2.94	2.94	2.93	2.92	2.90	2.89	2.88	2.87	2.87	2.86	2.86

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APPENDIX C

HYDROGEN CYANIDE DATA

TABLE C-1. HYDROGEN CYANIDE SAMPLE DATA AND CALCULATIONS

Lab No.	Sample Analyses* (µg/g) A1	A2	Calculations (A1-A2)	$\lvert(A1-A2)-(\overline{A1}-\overline{A2})\rvert$	(A1+A2)	$\lvert(A1+A2)-(\overline{A1}+\overline{A2})\rvert$
01†	0.3	0.3	0.0	0.08	0.6	0.1
02	0.1	0.1	0.0	0.08	0.2	0.3
04#	–	–	–	–	–	–
05	0.2	0.2	0.0	0.08	0.4	0.1
07#	–	–	–	–	–	–
08	0.3	0.2	0.1	0.02	0.5	0.0
09	0.2	0.2	0.0	0.08	0.4	0.1
10**	0.5	0.2	0.3	0.22	0.7	0.2
11	0.3	0.2	0.1	0.02	0.5	0.0
12	22.0	1.8	–	–	–	–
14†	0.4	0.3	0.1	0.02	0.7	0.2
Average††	0.29	0.21		$X_1 = 0.075$		$X_2 = 0.12$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.075\ (0.947) = 0.072$ µg/g††

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.072\ (3.26) = 0.23$ µg/g††

Coefficient of Repeatability = (0.23/0.25) x 100 = 92%††

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.10\ (0.947) = 0.095\ \mu g/g\dagger\dagger$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 0.095\ (3.01) = 0.29$ µg/g††

Coefficient of Reproducibility = (0.29/0.25) x 100 = 120%††

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Interference; no tube reading reported.
** Interference; tube reading distinct after 30 minutes.
†† Outlier values from Lab No. 12 have been excluded.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) A1	A3	Calculations (A1-A3)	|(A1-A3)-($\overline{A1}$-$\overline{A3}$)|	(A1+A3)	|(A1+A3)-($\overline{A1}$+$\overline{A3}$)|
01†	0.3	0.4	-0.1	0.1	0.7	0.12
02	0.1	0.0	0.1	0.1	0.1	0.48
04#	-	-	-	-	-	-
05	0.2	0.3	0.1	0.1	0.5	0.08
07#	-	-	-	-	-	-
08	0.3	0.2	0.1	0.1	0.5	0.08
09	0.2	0.3	0.1	0.1	0.5	0.08
10**	0.5	0.4	0.1	0.1	0.9	0.32
11	0.3	0.3	0.0	0.0	0.6	0.02
12	22.0	8.3	-	-	-	-
14†	0.4	0.4	0.0	0.0	0.8	0.22
Average††	0.29	0.29		X_1 = 0.075		X_2 = 0.18

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.075\ (0.947) = 0.072$ µg/g††

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.072\ (3.26) = 0.23$ µg/g††

Coefficient of Repeatability = (0.23/0.29) x 100 = 79%††

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.10\ (0.947) = 0.13\ \mu g/g††$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 0.13\ (3.13) = 0.41$ µg/g††

Coefficient of Reproducibility = (0.41/0.29) x 100 = 140%††

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Interference; no tube reading reported.
** Interference; tube reading distinct after 30 minutes.
†† Outlier values from Lab No. 12 have been excluded.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) A2	A3	Calculations (A2-A3)	$\lvert(A2-A3)-(\overline{A2}-\overline{A3})\rvert$	(A2+A3)	$\lvert(A2+A3)-(\overline{A2}+\overline{A3})\rvert$
01†	0.3	0.4	-0.1	0.02	0.7	0.2
02	0.1	0.0	0.1	0.18	0.1	0.4
04#	-	-	-	-	-	-
05	0.2	0.3	-0.1	0.02	0.5	0.0
07#	-	-	-	-	-	-
08	0.2	0.2	0.0	0.08	0.4	0.1
09	0.2	0.3	-0.1	0.02	0.5	0.0
10**	0.2	0.4	-0.2	0.06	0.6	0.1
11	0.2	0.3	-0.1	0.02	0.5	0.0
12	1.8	8.3	-	-	-	-
14†	0.3	0.4	-0.1	0.02	0.7	0.2
Average††	0.21	0.29		$X_1 = 0.052$		$X_2 = 0.125$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.052\ (0.947) = 0.049$ µg/g††

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.049\ (3.26) = 0.16$ µg/g††

Coefficient of Repeatability = (0.16/0.25) x 100 = 64%††

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.119\ (0.947) = 0.11\ \mu g/g††$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 0.11\ (3.13) = 0.34$ µg/g††

Coefficient of Reproducibility = (0.34/0.25) x 100 = 140%††

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Interference; no tube reading reported.
** Interference; tube reading distinct after 30 minutes.
†† Outlier values from Lab No. 12 have been excluded.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) B1	B2	Calculations (B1-B2)	$\lvert(B1-B2)-(\overline{B1}-\overline{B2})\rvert$	(B1+B2)	$\lvert(B1+B2)-(\overline{B1}+\overline{B2})\rvert$
01†	26.0	10.0	16.0	12.5	36.0	23.6
02	2.8	0.7	2.1	1.42	3.5	8.92
04	2.2	1.7	0.5	3.02	3.9	8.52
05	8.0	7.5	0.5	3.02	15.5	3.08
07	3.3	0.8	2.5	1.02	4.1	8.32
08	12.0	6.7	5.3	1.78	18.7	6.28
09	1.6	1.1	0.5	3.02	2.7	9.72
10#	11.0	10.0	1.0	2.52	21.0	8.58
11	7.9	7.3	0.6	2.92	15.2	2.78
12	4.1	0.8	3.3	0.22	4.9	7.52
14†	8.8	2.4	6.4	2.88	11.2	1.22
Average	7.97	4.45		$X_1 = 2.86$		$X_2 = 7.38$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 2.86\ (0.929) = 2.7\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 2.66\ (3.11) = 8.3\ \mu g/g$$

Coefficient of Repeatability = (8.27/6.21) x 100 = 130%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 5.60\ (0.929) = 5.2\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 5.20\ (3.03) = 16\ \mu g/g$$

Coefficient of Reproducibility = (15.8/6.21) x 100 = 250%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Interference; tube reading distinct after 30 minutes.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) B1	B3	Calculations (B1-B3)	|(B1-B3)-($\overline{B1}$-$\overline{B3}$)|	(B1+B3)	|(B1+B3)-($\overline{B1}$+$\overline{B3}$)|
01†	26.0	7.1	18.9	15.4	33.1	20.7
02	2.8	3.2	-0.4	3.95	6.0	6.39
04	2.2	2.0	0.2	3.35	4.2	8.19
05	8.0	5.9	2.1	1.45	13.9	1.51
07	3.3	1.8	1.5	2.05	5.1	7.29
08	12.0	7.5	4.5	0.95	19.5	7.11
09	1.6	1.6	0.0	3.55	3.2	9.19
10#	11.0	11.0	0.0	3.55	22.0	9.61
11	7.9	4.0	3.9	0.35	11.9	0.49
12	4.1	3.4	0.7	2.85	7.5	4.89
14†	8.8	1.1	7.7	4.15	9.9	2.49
Average	7.97	4.42		X_1 = 3.78		X_2 = 7.08

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 3.78\ (0.929) = 3.5\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 3.51\ (3.11) = 11\ \mu g/g$

Coefficient of Repeatability = (10.9/6.195) x 100 = 180%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 5.68\ (0.929) = 5.3\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 5.28\ (3.00) = 16\ \mu g/g$

Coefficient of Reproducibility = (15.8/6.195) x 100 = 260%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Interference; tube reading distinct after 30 minutes.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) B2	B3	Calculations (B2-B3)	|(B2-B3)-($\overline{B2}$-$\overline{B3}$)|	(B2+B3)	|(B2+B3)-($\overline{B2}$+$\overline{B3}$)|
01†	10.0	7.1	2.9	2.87	17.1	8.23
02	0.7	3.2	-2.5	2.53	3.9	4.97
04	1.7	2.0	-0.3	0.33	3.7	5.17
05	7.5	5.9	1.6	1.57	13.4	4.53
07	0.8	1.8	-1.0	1.03	2.6	6.27
08	6.7	7.5	-0.8	0.83	14.2	5.33
09	1.1	1.6	-0.5	0.47	2.7	6.17
10#	10.0	11.0	-1.0	1.03	21.0	12.1
11	7.3	4.0	3.3	3.27	11.3	2.43
12	0.8	3.4	-2.6	2.63	4.2	4.67
14†	2.4	1.1	1.3	1.37	3.5	5.37
Average	4.45	4.42		X_1 = 1.62		X_2 = 5.93

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 1.62\ (0.929) = 1.5\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 1.50\ (3.11) = 4.67\ \mu g/g$

Coefficient of Repeatability = (4.66/4.435) x 100 = 100%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 4.35\ (0.929) = 4.0\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 4.04\ (3.06) = 12.\ \mu g/g$

Coefficient of Reproducibility = (12.4/4.435) x 100 = 280%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Interference; tube reading distinct after 30 minutes.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) D1	D2	Calculations (D1-D2)	$\lvert(D1-D2)-(\overline{D1}-\overline{D2})\rvert$	(D1+D2)	$\lvert(D1+D2)-(\overline{D1}+\overline{D2})\rvert$
01†	8.2	4.2	4.0	3.05	12.4	7.69
02	0.1	0.0	0.1	0.85	0.1	4.61
04#	0.2	0.0	0.2	0.75	0.2	4.51
05	2.5	1.9	0.6	0.35	4.4	0.31
07	3.3	2.8	0.5	0.45	6.1	1.39
08	0.0	0.0	0.0	0.95	0.0	4.71
09	0.4	0.2	0.2	0.75	0.6	4.11
10**	6.2	5.8	0.4	0.55	12.0	7.29
11	2.7	2.1	0.6	0.35	4.8	0.09
12	1.4	1.2	0.2	0.75	2.6	2.11
14†	3.3	2.5	0.8	0.15	5.8	1.09
Average	2.83	1.88		$X_1 = 0.746$		$X_2 = 3.16$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.746\ (0.929) = 0.69\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.693\ (3.11) = 2.2\ \mu g/g$

Coefficient of Repeatability = (2.16/2.36) x 100 = 90%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 2.30\ (0.929) = 2.1\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 2.14\ (3.09) = 6.6\ \mu g/g$

Coefficient of Reproducibility = (6.61/2.36) x 100 = 280%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Diffuse front; difficult to read.
** Interference; tube difficult to read.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) D1	D3	Calculations (D1-D3)	$\lvert(D1-D3)-(\overline{D1}-\overline{D3})\rvert$	(D1+D3)	$\lvert(D1+D3)-(\overline{D1}+\overline{D3})\rvert$
01†	8.2	8.9	-0.7	1.11	17.1	12.2
02	0.1	0.0	0.1	0.31	0.1	4.83
04#	0.0	0.7	-0.7	1.11	0.7	4.23
05	2.5	2.0	0.5	0.09	4.5	0.43
07	3.3	3.0	0.3	0.11	6.3	1.37
08	0.0	0.0	0.0	0.41	0.0	4.93
09	0.4	0.6	-0.2	0.61	1.0	3.93
10**	6.2	1.8	4.4	3.99	8.0	3.07
11	2.7	3.8	-1.1	1.51	6.5	1.57
12††	-	-	-	-	-	-
14†	3.3	1.8	1.5	1.09	5.1	0.17
Average	2.67	2.26		$X_1 = 1.03$		$X_2 = 3.67$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 1.03\ (0.934) = 0.96\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.962\ (3.14) = 3.0\ \mu g/g$

Coefficient of Repeatability = (3.02/2.465) x 100 = 120%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 2.70\ (0.934) = 2.2\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 2.52\ (3.09) = 7.8\ \mu g/g$

Coefficient of Reproducibility = (7.79/2.465) x 100 = 320%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Diffuse front, difficult to read.
** Interference; tube difficult to read.
†† Insufficient sample; D3 measurement not performed.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) D2	D3	Calculations (D2-D3)	$\lvert(D2-D3)-(\overline{D2}-\overline{D3})\rvert$	(D2+D3)	$\lvert(D2+D3)-(\overline{D2}+\overline{D3})\rvert$
01†	4.2	8.9	-4.7	4.41	13.1	8.87
02	0.0	0.0	0.0	0.29	0.0	4.23
04#	0.2	0.7	-0.5	0.21	0.9	3.33
05	1.9	2.0	-0.1	0.19	3.9	0.33
07	2.8	3.0	-0.2	0.09	5.8	1.57
08	0.0	0.0	0.0	0.29	0.0	4.23
09	0.2	0.6	-0.4	0.11	0.8	3.43
10**	5.8	1.8	-1.7	1.41	5.9	1.67
11	2.1	3.8	-1.7	1.41	5.9	1.67
12††	-	-	-	-	-	-
14†	2.5	1.8	0.7	0.99	4.3	0.07
Average	1.97	2.26		$X_1 = 1.23$		$X_2 = 3.11$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 1.23\ (0.934) = 1.2\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 1.15\ (3.14) = 3.6\ \mu g/g$$

Coefficient of Repeatability = (3.61/2.115) x 100 = 170%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 2.36\ (0.934) = 2.2\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 2.20\ (3.06) = 6.7\ \mu g/g$$

Coefficient of Reproducibility = (6.73/2.115) x 100 = 320%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Diffuse front, difficult to read.
** Interference; tube difficult to read.
†† Insufficient sample; D3 measurement not performed.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) E1	E2	Calculations (E1-E2)	$\lvert(E1-E2)-(\overline{E1}-\overline{E2})\rvert$	(E1+E2)	$\lvert(E1+E2)-(\overline{E1}+\overline{E2})\rvert$
01†	0.9	0.9	0.0	0.5	1.8	0.76
02	0.7	0.2	0.5	0.0	0.9	1.66
04#	-	-	-	-	-	-
05	2.0	1.0	1.0	0.5	3.0	0.44
07	0.6	0.6	0.0	0.5	1.2	1.36
08	0.7	0.4	0.3	0.2	1.1	1.46
09	1.8	0.2	1.6	1.1	2.0	0.56
10**	1.1	0.7	0.4	0.1	1.8	0.76
11	1.8	1.5	0.3	0.2	3.3	0.74
12	3.3	2.8	0.5	0.0	6.1	3.54
14	2.4	2.0	0.4	0.1	4.4	1.84
Average	1.53	1.03		$X_1 = 0.32$		$X_2 = 1.31$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.32\ (0.934) = 0.30\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.299\ (3.14) = 0.94\ \mu g/g$

Coefficient of Repeatability = (0.939/1.28) x 100 = 73%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.954\ (0.934) = 0.89\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 0.891\ (3.11) = 2.8\ \mu g/g$

Coefficient of Reproducibility = (2.77/1.28) x 100 = 220%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
\# Interference; no tube reading reported.
** Interference; tube reading distinct after 30 minutes.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) E1	E3	Calculations (E1-E3)	$\lvert(E1-E3)-(\overline{E1}-\overline{E3})\rvert$	(E1+E3)	$\lvert(E1+E3)-(\overline{E1}+\overline{E3})\rvert$
01†	0.9	1.3	-0.4	0.43	1.2	1.83
02	0.7	0.3	0.4	0.37	1.0	2.03
04#	-	-	-	-	-	-
05	2.0	2.0	0.0	0.03	4.0	0.97
07	0.6	0.6	0.0	0.03	1.2	1.83
08	0.7	1.1	-.04	0.43	1.8	1.23
09	1.8	2.9	-1.1	1.13	4.7	1.67
10**	1.1	1.1	0.0	0.03	2.2	0.83
11	1.8	1.8	0.0	0.03	3.6	0.57
12	3.3	2.3	1.0	0.97	5.6	2.57
14	2.4	1.6	0.8	0.77	4.0	0.97
Average	1.53	1.50		$X_1 = 0.42$		$X_2 = 1.45$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 0.42\ (0.934) = 0.39\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 0.392\ (3.14) = 1.2\ \mu g/g$$

Coefficient of Repeatability = (1.23/1.515) x 100 = 81%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 1.07\ (0.934) = 1.0\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 1.00\ (3.09) = 3.1\ \mu g/g$$

Coefficient of Reproducibility = (3.09/1.515) x 100 = 200%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Interference; no tube reading reported.
** Interference; tube reading distinct after 30 minutes.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) E2	E3	Calculations (E2-E3)	|(E2-E3)-($\overline{E2}$-$\overline{E3}$)|	(E2+E3)	|(E2+E3)-($\overline{E2}$+$\overline{E3}$)|
01†	0.9	1.3	-0.4	0.07	2.2	0.33
02	0.2	0.3	-0.1	0.37	0.5	2.03
04#	-	-	-	-	-	-
05	1.0	2.0	-1.0	0.53	3.0	0.47
07	0.6	0.6	0.0	0.47	1.2	1.33
08	0.4	1.1	-0.7	0.23	1.5	1.03
09	0.2	2.9	-2.7	2.23	3.1	0.57
10**	0.7	1.1	-0.4	0.07	1.8	0.73
11	1.5	1.8	-0.3	0.17	3.3	0.77
12	2.8	2.3	0.5	0.97	5.1	2.57
14	2.0	1.6	0.4	0.87	3.6	1.07
Average	1.03	1.50		X_1 = 0.60		X_2 = 1.09

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.60\ (0.934) = 0.56\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.560\ (3.14) = 1.8\ \mu g/g$

Coefficient of Repeatability = (1.76/1.265) x 100 = 140%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.880\ (0.934) = 0.82\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 0.822\ (3.02) = 2.5\ \mu g/g$

Coefficient of Reproducibility = (2.48/1.265) x 100 = 200%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube initially red-orange, difficult to read.
# Interference; no tube reading reported.
** Interference; tube reading distinct after 30 minutes.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) F1	F2	Calculations (F1-F2)	$\lvert(F1-F2)-(\overline{F1}-\overline{F2})\rvert$	(F1+F2)	$\lvert(F1+F2)-(\overline{F1}+\overline{F2})\rvert$
01	0.0	0.0	0.0	0.07	0.0	0.29
02	0.0	0.0	0.0	0.07	0.0	0.29
04	0.8	0.4	0.4	0.33	1.2	0.91
05	0.0	0.0	0.0	0.07	0.0	0.29
07	0.0	0.0	0.0	0.07	0.0	0.29
08	0.3	0.0	0.3	0.23	0.3	0.01
09	0.4	0.4	0.0	0.07	0.8	0.51
10	0.0	0.0	0.0	0.07	0.0	0.29
11	0.3	0.3	0.0	0.07	0.6	0.31
12	0.0	0.0	0.0	0.07	0.0	0.29
14†	-	-	-	-	-	-
Average	0.18	0.11		$X_1 = 0.112$		$X_2 = 0.348$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 0.112\ (0.934) = 0.10\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 0.105\ (3.14) = 0.33\ \mu g/g$$

Coefficient of Repeatability = (0.330/0.145) x 100 = 230%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.258\ (0.934) = 0.24\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 0.241\ (3.09) = 0.74\ \mu g/g$$

Coefficient of Reproducibility = (0.745/0.145) x 100 = 510%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube red-orange to yellow, no reading reported.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) F1	F3	Calculations (F1-F3)	$\lvert(F1-F3)-(\overline{F1}-\overline{F3})\rvert$	(F1+F3)	$\lvert(F1+F3)-(\overline{F1}+\overline{F3})\rvert$
01	0.0	0.2	-0.1	0.25	0.2	0.11
02	0.0	0.0	0.0	0.05	0.0	0.31
04	0.8	0.2	0.6	0.55	1.0	0.69
05	0.0	0.0	0.0	0.05	0.0	0.31
07	0.0	0.0	0.0	0.05	0.0	0.31
08	0.3	0.0	0.3	0.25	0.3	0.01
09	0.4	0.0	0.04	0.35	0.4	0.09
10	0.0	0.0	0.0	0.05	0.0	0.31
11	0.3	0.3	0.0	0.05	0.6	0.29
12	0.0	0.6	-0.6	0.65	0.6	0.29
14†	-	-	-	-	-	-
Average	0.18	0.13		$X_1 = 0.23$		$X_2 = 0.27$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.23\ (0.934) = 0.22\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.215\ (3.14) = 0.68\ \mu g/g$

Coefficient of Repeatability = (0.675/0.155) x 100 = 440%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.251\ (0.934) = 0.23\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 0.234\ (2.96) = 0.69\ \mu g/g$

Coefficient of Reproducibility = (0.693/0.155) x 100 = 450%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube red-orange to yellow, no reading reported.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) F2	F3	Calculations (F2-F3)	$\lvert(F2-F3)-(\overline{F2}-\overline{F3})\rvert$	(F2+F3)	$\lvert(F2+F3)-(\overline{F2}+\overline{F3})\rvert$
01	0.0	0.2	-0.2	0.18	0.2	0.04
02	0.0	0.0	0.0	0.02	0.0	0.24
04	0.4	0.2	0.2	0.22	0.6	0.36
05	0.0	0.0	0.0	0.02	0.0	0.24
07	0.0	0.0	0.0	0.02	0.0	0.24
08	0.0	0.0	0.0	0.02	0.0	0.24
09	0.4	0.0	0.4	0.42	0.4	0.16
10	0.0	0.0	0.0	0.02	0.0	0.24
11	0.3	0.3	0.0	0.02	0.6	0.36
12	0.0	0.6	-0.6	0.58	0.6	0.36
14†	-	-	-	-	-	-
Average	0.11	0.13		$X_1 = 0.152$		$X_2 = 0.248$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.152\ (0.934) = 0.14\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.142\ (3.14) = 0.45\ \mu g/g$

Coefficient of Repeatability = (0.446/0.12) x 100 = 370%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.206\ (0.934) = 0.19\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 0.192\ (3.00) = 0.58\ \mu g/g$

Coefficient of Reproducibility = (0.576/0.12) x 100 = 480%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube red-orange to yellow, no reading reported.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) G1	G2	Calculations (G1-G2)	$\lvert(G1-G2)-(\overline{G1}-\overline{G2})\rvert$	(G1+G2)	$\lvert(G1+G2)-(\overline{G1}+\overline{G2})\rvert$
01†	17.0	2.2	14.8	12.2	19.2	13.37
02	0.0	0.0	0.0	2.65	0.0	5.83
04	0.0	0.0	0.0	2.65	0.0	5.83
05	3.3	3.2	0.1	2.55	6.5	0.67
07	1.4	1.2	0.2	2.45	2.6	3.23
08	0.0	0.0	0.0	2.65	0.0	5.83
09	1.1	0.6	0.5	2.15	1.7	4.13
10#	2.7	0.0	2.7	0.05	2.7	3.13
11	6.2	5.9	0.3	2.35	12.1	6.27
12	3.9	3.3	0.6	2.05	7.2	1.37
14†	11.0	1.1	9.9	7.25	12.1	6.27
Average	4.24	1.59		$X_1 = 3.54$		$X_2 = 5.08$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 3.54\ (0.929) = 3.3\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 3.29\ (3.11) = 10\ \mu g/g$

Coefficient of Repeatability = (10.2/2.915) x 100 = 350%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 4.38\ (0.929) = 4.1\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 4.07\ (2.96) = 12\ \mu g/g$

Coefficient of Reproducibility = (12.0/2.915) x 100 = 410%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube red-orange and difficult to read.
# Interference; tube difficult to read.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) G1	G3	Calculations (G1-G3)	|(G1-G3)-($\overline{G1}$-$\overline{G3}$)|	(G1+G3)	|(G1+G3)-($\overline{G1}$+$\overline{G3}$)|
01†	17.0	6.6	10.4	8.54	23.6	16.0
02	0.0	0.0	0.0	1.86	0.0	7.62
04	0.0	0.0	0.0	1.86	0.0	7.62
05	3.3	3.7	-0.4	2.26	7.0	0.62
07	1.4	1.1	0.3	1.56	2.5	5.12
08#	-	-	-	-	-	-
09	1.1	0.4	0.7	1.16	1.5	6.12
10**	2.7	4.6	-1.9	3.76	7.3	0.32
11	6.2	6.4	-0.2	2.06	12.6	4.98
12#	-	-	-	-	-	-
14†	11.0	3.1	7.7	6.04	14.1	6.48
Average	4.74	2.88		X_1 = 3.23		X_2 = 6.10

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 3.23\ (0.940) = 3.0\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 3.04\ (3.20) = 9.7\ \mu g/g$

Coefficient of Repeatability = (9.73/3.81) x 100 = 260%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 4.88\ (0.940) = 4.6\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 4.59\ (3.06) = 14\ \mu g/g$

Coefficient of Reproducibility = (14.0/3.81) x 100 = 370%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube red-orange and difficult to read.
# Insufficient sample; G3 measurement not performed.
** Interference; tube difficult to read.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) G2	G3	Calculations (G2-G3)	$\lvert(G2-G3)-(\overline{G2}-\overline{G3})\rvert$	(G2+G3)	$\lvert(G2+G3)-(\overline{G2}+\overline{G3})\rvert$
01†	2.2	6.6	-4.4	3.1	8.8	4.34
02	0.0	0.0	0.0	1.3	0.0	4.46
04	0.0	0.0	0.0	1.3	0.0	4.46
05	3.2	3.7	-0.5	0.8	6.9	2.44
07	1.2	1.1	0.1	1.4	2.3	2.16
08#	-	-	-	-	-	-
09	0.6	0.4	0.2	1.5	1.0	3.46
10**	0.0	4.6	-4.6	3.3	4.6	0.14
11	5.9	6.4	-0.5	0.8	12.3	7.84
12#	-	-	-	-	-	-
14†	1.1	3.1	-2.0	0.7	4.2	0.26
Average	1.58	2.88		$X_1 = 1.58$		$X_2 = 3.28$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 1.58\ (0.940) = 1.5\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 1.48\ (3.20) = 4.7\ \mu g/g$

Coefficient of Repeatability = (4.74/2/23) x 100 = 210%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 2.57\ (0.940) = 2.4\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 2.42\ (3.06) = 7.4\ \mu g/g$

Coefficient of Reproducibility = (7.41/2.23) x 100 = 330%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; tube red-orange and difficult to read.
# Insufficient sample; G3 measurement not performed.
** Interference; tube difficult to read.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) H1	H2	Calculations (H1-H2)	|(H1-H2)-($\overline{H1-H2}$)|	(H1+H2)	|(H1+H2)-($\overline{H1+H2}$)|
01	0.0	0.0	0.0	0.27	0.0	2.69
02	0.7	0.7	0.0	0.27	1.4	1.29
04†	-	-	-	-	-	-
05	1.0	1.0	0.0	0.27	2.0	0.69
07	0.7	0.6	0.1	0.17	1.3	1.39
08	1.1	0.9	0.2	0.07	2.0	0.69
09	2.8	2.2	0.6	0.33	5.0	2.31
10#	0.7	0.7	0.0	0.27	1.4	1.29
11	2.0	1.5	0.5	0.23	3.5	0.81
12	2.5	1.7	0.8	0.53	4.2	1.51
14**	3.3	2.8	0.5	0.23	6.1	3.41
Average	1.48	1.21		$X_1 = 0.264$		$X_2 = 1.61$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 0.264\ (0.934) = 0.25\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 0.246\ (3.14) = 0.77\ \mu g/g$$

Coefficient of Repeatability = (0.772/1.345) x 100 = 57%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 1.15\ (0.934) = 1.1\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 1.07\ (3.12) = 3.3\ \mu g/g$$

Coefficient of Reproducibility = (3.34/1.345) x 100 = 250%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; no tube reading reported.
# Interference; tube reading distinct after 30 minutes.
** Interference; tube initially red-orange.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) H2	H3	Calculations (H2-H3)	$\lvert(H2-H3)-(\overline{H2}-\overline{H3})\rvert$	(H2+H3)	$\lvert(H2+H3)-(\overline{H2}+\overline{H3})\rvert$
01	0.0	0.9	-0.9	0.94	0.0	1.56
02	0.7	0.7	0.0	0.04	1.4	1.06
04†	-	-	-	-	-	-
05	1.0	1.0	0.0	0.04	2.0	0.46
07	0.6	0.6	0.0	0.04	1.2	1.26
08	0.9	0.9	0.0	0.04	1.8	0.66
09	2.2	2.0	0.2	0.16	4.2	1.74
10#	0.7	1.3	-0.6	0.64	2.0	0.46
11	1.5	1.0	0.5	0.46	2.5	0.04
12	1.7	2.1	-0.4	0.44	3.8	1.34
14**	2.8	2.0	0.8	0.76	4.8	2.34
Average	1.21	1.25		$X_1 = 0.356$		$X_2 = 1.09$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 0.356\ (0.934) = 0.33\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 0.332\ (3.14) = 1.0\ \mu g/g$$

Coefficient of Repeatability = (1.04/1.23) x 100 = 85%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.811\ (0.934) = 0.76\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 0.757\ (3.09) = 2.3\ \mu g/g$$

Coefficient of Reproducibility = (2.34/1.23) x 100 = 190%

(continued)

* Sample identification (by letter) and analysis number.
† Interference; no tube reading reported.
# Interference; tube reading distinct after 30 minutes.
** Interference; tube initially red-orange.

TABLE C-1. (Continued)

Lab No.	Sample Analyses* (µg/g) H1	H3	Calculations (H1-H3)	$\lvert(H1-H3)-(\overline{H1}-\overline{H3})\rvert$	(H1+H3)	$\lvert(H1+H3)-(\overline{H1}+\overline{H3})\rvert$
01	0.0	0.9	-0.9	1.13	0.9	1.83
02	0.7	0.7	0.0	0.23	1.4	1.33
04†	-	-	-	-	-	-
05	1.0	1.0	0.0	0.23	2.0	0.73
07	0.7	0.6	0.1	0.13	1.3	1.43
08	1.1	0.9	0.2	0.03	2.0	0.73
09	2.8	2.0	0.8	0.57	4.8	2.07
10#	0.7	1.3	-0.6	0.83	2.0	0.73
11	2.0	1.0	1.0	0.77	3.0	0.27
12	2.5	2.1	0.4	0.17	4.6	1.87
14**	3.3	2.0	1.3	1.07	5.3	2.57
Average	1.48	1.25		$X_1 = 0.516$		$X_2 = 1.36$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.516\ (0.934) = 0.48\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.482\ (3.14) = 1.5\ \mu g/g$

Coefficient of Repeatability = (1.51/1.365) x 100 = 110%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 1.03\ (0.934) = 0.96\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 0.962\ (3.06) = 2.9\ \mu g/g$

Coefficient of Reproducibility = (0.962/1.365) x 100 = 220%

* Sample identification (by letter) and analysis number.
† Interference; no tube reading reported.
\# Interference; tube reading distinct after 30 minutes.
** Interference; tube initially red-orange.

APPENDIX D

HYDROGEN SULFIDE DATA

TABLE D-1. HYDROGEN SULFIDE SAMPLE DATA AND CALCULATIONS

Lab No.	Sample Analyses* (µg/g) A1	A2	Calculations (A1-A2)	$\lvert(A1-A2)-(\overline{A1}-\overline{A2})\rvert$	(A1+A2)	$\lvert(A1+A2)-(\overline{A1}+\overline{A2})\rvert$
01	0.0	0.0	0.0	0.07	0.0	0.89
02	0.0	0.0	0.0	0.07	0.0	0.89
04	0.1	0.0	0.1	0.03	0.1	0.79
05	1.0	1.0	0.0	0.07	2.0	1.11
06	0.7	0.7	0.0	0.07	1.4	0.51
07	0.7	0.6	0.1	0.03	1.3	0.41
08	0.0	0.0	0.0	0.07	0.0	0.89
09	1.8	1.7	0.1	0.03	3.5	2.61
10	1.4	0.9	0.5	0.43	2.3	1.41
11	0.0	0.0	0.0	0.07	0.0	0.89
12	0.0	0.0	0.0	0.07	0.0	0.89
14	0.0	0.0	0.0	0.07	0.0	0.89
Average	0.48	0.41		$X_1 = 0.090$		$X_2 = 1.02$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 0.090\ (0.925) = 0.083\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 0.083\ (3.08) = 0.26\ \mu g/g$$

Coefficient of Repeatability = (0.256/0.445) x 100 = 58%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.724\ (0.925) = 0.670\ \mu g/g$$

Estimate of Reproducibility:

$$R_1 = S_2K_3 = 0.670\ (3.07) = 2.1\ \mu g/g$$

Coefficient of Reproducibility = (2.06/0.445) x 100 = 460%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) A2	A3	Calculations (A2-A3)	$\lvert(A2-A3)-(\overline{A2}-\overline{A3})\rvert$	(A2+A3)	$\lvert(A2+A3)-(\overline{A2}+\overline{A3})\rvert$
01	0.0	1.1	-1.1	0.95	1.1	0.13
02	0.0	0.0	0.0	0.15	0.0	0.97
04	0.0	0.0	0.0	0.15	0.0	0.97
05	1.0	0.3	0.7	0.85	1.3	0.33
06	0.7	0.6	0.1	0.25	1.3	0.33
07	0.6	1.8	-1.2	1.05	2.4	1.43
08	0.0	0.0	0.0	0.15	0.0	0.97
09	1.7	0.4	1.3	1.45	2.1	1.13
10	0.9	2.5	-1.6	1.45	3.4	2.43
11	0.0	0.0	0.0	0.15	0.0	0.97
12	0.0	0.0	0.0	0.15	0.0	0.97
14	0.0	0.0	0.0	0.15	0.0	0.97
Average	0.41	0.56		$X_1 = 0.575$		$X_2 = 0.967$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.575\ (0.925) = 0.53\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.532\ (3.08) = 1.6\ \mu g/g$

Coefficient of Repeatability = (1.64/0.485) x 100 = 340%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.796\ (0.925) = 0.74\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 0.736\ (2.95) = 2.2\ \mu g/g$

Coefficient of Reproducibility = (2.17/0.485) x 100 = 450%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) A1	A3	Calculations (A1-A3)	$\lvert(A1-A3)-(\overline{A1}-\overline{A3})\rvert$	(A1+A3)	$\lvert(A1+A3)-(\overline{A1}+\overline{A3})\rvert$
01	0.0	1.1	-1.1	1.02	1.1	0.06
02	0.0	0.0	0.0	0.08	0.0	1.04
04	0.1	0.0	0.1	0.18	0.1	0.94
05	1.0	0.3	0.7	0.78	1.3	0.26
06	0.7	0.6	0.1	0.18	1.3	0.26
07	0.7	1.8	-1.1	1.02	2.5	1.46
08	0.0	0.0	0.0	0.08	0.0	1.04
09	1.8	0.4	1.4	1.48	2.2	1.16
10	1.4	2.5	-1.1	1.01	3.9	2.86
11	0.0	0.0	0.0	0.08	0.0	1.04
12	0.0	0.0	0.0	0.08	0.0	1.04
14	0.0	0.0	0.0	0.08	0.0	1.04
Average	0.48	0.56		$X_1 = 0.507$		$X_2 = 1.02$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.507\ (0.925) = 0.47\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.469\ (3.08) = 1.4\ \mu g/g$

Coefficient of Repeatability = (1.44/0.52) x 100 = 280%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.805\ (0.925) = 0.74\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 0.745\ (2.98) = 2.2\ \mu g/g$

Coefficient of Reproducibility = (2.22/0.52) x 100 = 430%

(continued)

*Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) B1	B2	Calculations (B1-B2)	$\lvert(B1-B2)-(\overline{B1}-\overline{B2})\rvert$	(B1+B2)	$\lvert(B1+B2)-(\overline{B1}+\overline{B2})\rvert$
01	7.3	6.3	1.0	0.81	13.6	7.73
02	0.0	0.0	0.0	0.19	0.0	5.87
04	0.0	0.0	0.0	0.19	0.0	5.87
05	9.7	9.3	0.4	0.21	19.0	13.1
06	6.6	6.6	0.0	0.19	13.2	7.33
07	0.1	0.0	0.1	0.09	0.1	5.77
08	0.0	0.0	0.0	0.19	0.0	5.87
09	0.3	0.1	0.2	0.01	0.4	5.47
10	8.7	8.4	0.3	0.11	17.1	11.2
11	3.5	3.2	0.3	0.11	6.7	0.83
12	0.0	0.0	0.0	0.19	0.0	5.87
14	0.2	0.2	0.0	0.19	0.4	5.47
Average	3.03	2.84		$X_1 = 0.207$		$X_2 = 6.70$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 0.207\ (0.925) = 0.19\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.191\ (3.08) = 0.59\ \mu g/g$

Coefficient of Repeatability = (0.588/2.935) x 100 = 20%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 4.74\ (0.925) = 4.4\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 4.38\ (3.08) = 14\ \mu g/g$

Coefficient of Reproducibility = (13.5/2.935) x 100 = 460%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) B2	B3	Calculations (B2-B3)	$\lvert(B2-B3)-(\overline{B2}-\overline{B3})\rvert$	(B2+B3)	$\lvert(B2+B3)-(\overline{B2}+\overline{B3})\rvert$
01	6.3	5.0	1.3	0.10	11.3	7.02
02	0.0	0.3	-0.3	1.70	0.3	3.98
04	0.0	0.1	-0.1	1.50	0.1	4.18
05	9.3	4.0	5.3	3.90	13.3	9.02
06	6.6	2.8	-3.8	5.20	9.4	5.12
07	0.0	0.3	-0.3	1.70	0.3	3.98
08	0.0	0.1	0.0	1.40	0.0	4.28
09	0.1	0.0	0.0	1.40	0.1	4.18
10	8.4	3.8	4.6	3.20	12.2	7.92
11	3.2	0.6	2.6	1.20	3.8	0.48
12	0.0	0.0	0.0	1.40	0.0	4.28
14	0.2	0.3	-0.1	1.50	0.5	3.78
Average	2.84	1.44		$X_1 = 2.02$		$X_2 = 4.85$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 2.02\ (0.925) = 1.87\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 1.87\ (3.08) = 5.8\ \mu g/g$

Coefficient of Repeatability = (5.76/2.14) x 100 = 270%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 3.72\ (0.925) = 3.4\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 3.44\ (3.00) = 10\ \mu g/g$

Coefficient of Reproducibility = (10.3/2.14) x 100 = 480%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) B1	B3	Calculations (B1-B3)	$\lvert(B1-B3)-(\overline{B1}-\overline{B3})\rvert$	(B1+B3)	$\lvert(B1+B3)-(\overline{B1}+\overline{B3})\rvert$
01	7.3	5.0	2.3	0.71	12.3	7.83
02	0.0	0.3	-0.3	1.89	0.3	4.17
04	0.0	0.1	-0.1	1.69	0.1	4.37
05	9.7	4.0	5.7	4.11	13.7	9.23
06	6.6	2.8	3.8	2.21	9.4	4.93
07	0.1	0.3	-0.2	1.79	0.4	4.07
08	0.0	0.0	0.0	1.59	0.0	4.47
09	0.3	0.0	0.3	1.29	0.3	4.17
10	8.7	3.8	4.9	3.31	12.5	8.03
11	3.5	0.6	2.9	1.31	4.1	0.37
12	0.0	0.0	0.0	1.59	0.0	4.47
14	0.2	0.3	-0.1	1.69	0.5	3.97
Average	3.03	1.44		$X_1 = 1.93$		$X_2 = 5.01$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 1.93\ (0.925) = 1.8\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 1.78\ (3.08) = 5.5\ \mu g/g$

Coefficient of Repeatability = (5.48/2.235) x 100 = 240%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 3.80\ (0.925) = 3.5\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 3.52\ (3.00) = 11\ \mu g/g$

Coefficient of Reproducibility = (10.6/2.235) x 100 = 470%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) D1	D2	(D1-D2)	$\lvert(D1-D2)-(\overline{D1}-\overline{D2})\rvert$	(D1+D2)	$\lvert(D1+D2)-(\overline{D1}+\overline{D2})\rvert$
01	531	507	24	28	1038	220
02	279	269	10	42	548	270
04	389	247	142	90	636	182
05	290	250	40	12	540	278
06	448	448	0	52	896	78
07	473	399	74	22	872	54
08	602	518	84	32	1120	302
09	266	182	84	32	448	370
10	475	424	51	1	899	81
11	474	438	36	16	912	94
12	491	479	12	40	970	152
14	504	432	72	20	936	118
Average	435	383		$X_1 = 32.2$		$X_2 = 183$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 32.2\ (0.925) = 30\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 29.8\ (3.08) = 92\ \mu g/g$$

Coefficient of Repeatability = (91.8/409) x 100 = 22%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 131\ (0.925) = 120\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 121\ (3.05) = 370\ \mu g/g$$

Coefficient of Reproducibility = (369/409) x 100 = 90%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) D1	D3	Calculations (D1-D3)	$\lvert(D1-D3)-(\overline{D1}-\overline{D3})\rvert$	(D1+D3)	$\lvert(D1+D3)-(\overline{D1}+\overline{D3})\rvert$
01	531	420	111	104	951	88
02	279	262	17	10	541	322
04	389	363	26	19	752	111
05	290	330	-40	47	620	243
06	448	390	58	51	838	25
07	473	367	106	99	840	23
08	602	490	112	105	1092	229
09	266	658	-392	399	924	61
10	475	476	-1	8	951	88
11	474	400	74	67	874	11
12	491	349	142	135	840	23
14	504	628	-124	131	1132	269
Average	435	428		$X_1 = 97.9$		$X_2 = 124$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 97.9\ (0.925) = 91\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 90.6\ (3.08) = 280\ \mu g/g$$

Coefficient of Repeatability = (279/431/5) x 100 = 65%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 112\ (0.925) = 100\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 104\ (2.93) = 300\ \mu g/g$$

Coefficient of Reproducibility = (305/431.5) x 100 = 71%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) D2	D3	Calculations (D2-D3)	$\lvert(D2-D3)-(\overline{D2}-\overline{D3})\rvert$	(D2+D3)	$\lvert(D2+D3)-(\overline{D2}+\overline{D3})\rvert$
01	507	420	87	133	927	117
02	269	262	7	53	531	279
04	247	363	-116	70	610	200
05	250	330	-80	34	580	230
06	448	390	58	104	838	28
07	399	367	32	78	766	44
08	518	490	28	74	1008	198
09	182	658	-476	430	840	30
10	424	476	-52	6	900	90
11	438	400	38	84	838	28
12	479	349	130	176	828	18
14	432	628	-196	150	1060	250
Average	382	428		$X_1 = 116$		$X_2 = 126$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 116\ (0.925) = 110\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 107\ (3.08) = 330\ \mu g/g$$

Coefficient of Repeatability = (330/405) x 100 = 82%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 121\ (0.925) = 110\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 112\ (2.92) = 330\ \mu g/g$$

Coefficient of Reproducibility = (327/405) x 100 = 81%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) E1	E2	(E1-E2)	$\lvert(E1-E2)-(\overline{E1}-\overline{E2})\rvert$	(E1+E2)	$\lvert(E1+E2)-(\overline{E1}+\overline{E2})\rvert$
01	4.2	3.8	0.4	0.23	8.0	0.39
02	4.5	3.4	1.1	0.47	7.9	0.29
04	2.8	2.1	0.7	0.07	4.9	2.71
05	2.7	2.2	0.5	0.13	4.9	2.71
06	4.5	3.5	1.0	0.37	8.0	0.39
07	3.9	3.1	0.8	0.17	7.0	0.61
08	3.6	3.5	0.1	0.53	7.1	0.51
09	4.9	3.8	1.1	0.47	8.7	1.09
10	3.5	2.7	0.8	0.17	6.2	1.41
11	4.5	4.1	0.4	0.23	8.6	0.99
12	5.6	5.5	0.1	0.53	11.1	3.49
14	4.8	4.2	0.6	0.03	9.0	1.39
Average	4.12	3.49		$X_1 = 0.283$		$X_2 = 1.33$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 0.283\ (0.925) = 0.26\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 0.261\ (3.08) = 0.80\ \mu g/g$$

Coefficient of Repeatability = (0.804/3.805) x 100 = 21%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 0.962\ (0.925) = 0.89\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 0.890\ (3.05) = 2.7\ \mu g/g$$

Coefficient of Reproducibility = (2.71/3.805) x 100 = 57%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) E2	E3	Calculations (E2-E3)	$\lvert(E2-E3)-(\overline{E2}-\overline{E3})\rvert$	(E2+E3)	$\lvert(E2+E3)-(\overline{E2}+\overline{E3})\rvert$
01	3.8	3.9	-0.1	0.04	7.7	0.58
02	3.4	3.2	0.2	0.34	6.6	0.52
04	2.1	3.5	-1.4	1.26	5.6	1.52
05	2.2	2.7	-0.5	0.36	4.9	2.22
06	3.5	5.0	-1.5	1.36	8.5	1.38
07	3.1	2.8	0.3	0.44	5.9	1.22
08	3.5	4.4	-0.9	0.76	7.9	0.78
09	3.8	2.0	1.8	1.94	5.8	1.32
10	2.7	3.2	0.5	0.64	5.9	1.22
11	4.1	4.5	0.4	0.54	8.6	1.48
12	5.5	2.2	3.3	3.44	7.7	0.58
14	4.2	6.2	-2.0	1.86	10.4	3.28
Average	3.49	3.63		$X_1 = 1.08$		$X_2 = 1.34$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 1.08\ (0.925) = 1.0\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.999\ (3.08) = 3.1\ \mu g/g$

Coefficient of Repeatability = (3.08/3.56) x 100 = 86%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 1.22\ (0.925) = 1.1\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3\ 1.13\ (2.93) = 3.3\ \mu g/g$

Coefficient of Reproducibility = (3.31/3.56) x 100 = 93%

(continued)

* Sample identification (by letter) and analysis number.

* TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) E1	E3	Calculations (E1-E3)	$\lvert(E1-E3)-(\overline{E1}-\overline{E3})\rvert$	(E1+E3)	$\lvert(E1+E2)-(\overline{E1}+\overline{E2})\rvert$
01	4.2	3.9	0.3	0.19	8.1	0.35
02	4.5	3.2	1.3	0.81	7.7	0.05
04	2.8	3.5	-0.7	0.21	6.3	1.45
05	2.7	2.7	0.0	0.49	5.4	2.35
06	4.5	5.0	-0.5	0.99	9.5	1.75
07	3.9	2.8	1.1	0.61	6.7	1.05
08	3.6	4.4	-0.8	1.29	8.0	0.25
09	4.9	2.0	2.9	2.41	6.9	0.85
10	3.5	3.2	0.3	0.19	6.7	1.05
11	4.5	4.5	0.0	0.49	9.0	1.25
12	5.6	2.2	3.4	2.91	7.8	0.05
14	4.8	6.2	-1.4	1.89	11.0	3.25
Average	4.12	3.63		$X_1 = 1.04$		$X_2 = 1.14$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 1.04\ (0.925) = 0.96\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 0.962\ (3.08) = 3.0\ \mu g/g$

Coefficient of Repeatability = (2.96/3.875) x 100 = 76%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 1.09\ (0.925) = 1.0\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 1.01\ (2.92) = 3.0\ \mu g/g$

Coefficient of Reproducibility = (2.95/3.875) x 100 = 76%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) F1	F2	Calculations (F1-F2)	$\lvert(F1-F2)-(\overline{F1}-\overline{F2})\rvert$	(F1+F2)	$\lvert(F1+F2)-(\overline{F1}+\overline{F2})\rvert$
01†	-	-	-	-	-	-
02	584	445	139	125	1029	697
04	1808	1600	208	56	3408	1682
05	104	94	10	254	198	1528
06	700	600	100	164	1300	426
07	350	336	14	250	686	1040
08	1122	623	499	235	1745	19
09	1344	1249	95	169	2593	867
10	1909	1080	829	565	2989	1263
11	918	910	8	256	1828	102
12	1056	807	249	15	1863	137
14	1051	296	755	491	1347	379
Average	995	731		X_1 = 234		X_2 = 740

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 234\ (0.929) = 220\ \mu g/g$

Estimate of Repeatability:

$R_1 = S_1K_2 = 217\ (3.11) = 680\ \mu g/g$

Coefficient of Repeatability = (675/863) x 100 = 78%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 549\ (0.929) = 510\ \mu g/g$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 510\ (3.06) = 1600\ \mu g/g$

Coefficient of Reproducibility = (1561/863) x 100 = 180%

(continued)

* Sample identification (by letter) and analysis number.
† Tube readings were off scale; no measurements were reported.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) F2	F3	Calculations (F2-F3)	$\lvert(F2-F3)-(\overline{F2}-\overline{F3})\rvert$	(F2+F3)	$\lvert(F2+F3)-(\overline{F2}+\overline{F3})\rvert$
01†	-	-	-	-	-	-
02	445	124	321	478	569	1020
04	1600	1018	582	709	2618	1029
05	94	120	-26	101	214	1375
06	600	2100	-1500	1373	2700	1111
07	336	182	154	281	518	1071
08	623	672	-49	78	1395	194
09	1249	1204	45	172	2453	864
10	1080	1027	53	180	2107	518
11	910	927	-17	110	1837	248
12	807	1712	-905	778	2519	930
14	296	360	-64	63	656	933
Average	731	858		$X_1 = 390$		$X_2 = 845$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 390\ (0.929) = 360\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 362\ (3.11) = 1100\%$$

Coefficient of Repeatability = (1126/794.5) x 100 = 140%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 659\ (0.929) = 610\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 611\ (3.00) = 1800\ \mu g/g$$

Coefficient of Reproducibility = (1833/794.5) x 100 = 230%

(continued)

* Sample identification (by letter) and analysis number.
† Tube readings were off scale; no measurements were reported.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) F1	F3	Calculations (F1-F3)	$\lvert(F1-F3)-(\overline{F1}-\overline{F3})\rvert$	(F1+F3)	$\lvert(F1+F3)-(\overline{F1}+\overline{F3})\rvert$
01†	-	-	-	-	-	-
02	584	124	460	323	708	1145
04	1808	1018	790	653	2826	973
05	104	120	-16	153	224	1629
06	700	2100	-1300	1437	2800	947
07	350	182	168	31	532	1321
08	1122	672	450	313	1794	59
09	1344	1204	140	3	1548	305
10	1909	1027	882	745	2936	1083
11	918	927	-9	146	1845	8
12	1056	1712	-656	793	2768	915
14	1051	360	691	554	1411	442
Average	995	858		$X_1 = 468$		$X_2 = 802$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 468\ (0.929) = 440\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 435\ (3.11) = 1400\ \mu g/g$$

Coefficient of Repeatability = (1353/962.5) x 100 = 150%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 657\ (0.929) = 610\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 610\ (2.98) = 1800\ \mu g/g$$

Coefficient of Reproducibility = (1818/926.5) x 100 = 200%

(continued)

* Sample identification (by letter) and analysis number.
† Tube readings were off scale; no measurements were reported.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) G1	G2	Calculations (G1-G2)	$\lvert(G1-G2)-(\overline{G1}-\overline{G2})\rvert$	(G1+G2)	$\lvert(G1+G2)-(\overline{G1}+\overline{G2})\rvert$
01	541	284	257	145	825	97
02	332	258	74	38	590	138
04	135	60	75	37	195	533
05	310	240	70	42	550	178
06	530	450	80	32	980	252
07	98	42	56	56	140	588
08	672	574	98	14	1246	518
09	350	294	56	56	644	84
10	464	372	92	105	836	108
11	532	504	28	84	1036	308
12	379	163	216	104	542	186
14	700	459	241	129	1159	431
Average	420	308		$X_1 = 70.2$		$X_2 = 285$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 70.2\ (0.925) = 65\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 64.9\ (3.08) = 200\ \mu g/g$$

Coefficient of Repeatability = (200/364) x 100 = 55%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 208\ (0.925) = 190\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 192\ (3.04) = 580\ \mu g/g\ H2S$$

Coefficient of Reproducibility = (584/364) x 100 = 160%

(continued)

* Sample identification (by letter) and analysis number.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (μg/g) G1	G3	Calculations (G1-G3)	$\lvert(G1-G3)-(\overline{G1}-\overline{G3})\rvert$	(G1+G3)	$\lvert(G1+G3)-(\overline{G1}+\overline{G3})\rvert$
01	541	616	-75	130	1157	356
02†	-	-	-	-	-	-
04	135	45	90	35	180	621
05	310	310	0	55	620	181
06	530	520	10	45	1050	249
07	98	84	14	41	182	619
08	672	840	-168	223	1512	711
	350	140	210	155	490	311
10	464	383	81	26	847	46
11	532	532	0	55	1064	263
12	379	99	280	225	478	323
14	700	536	164	109	1236	435
Average	428	373		$X_1 = 99.9$		$X_2 = 374$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 99.9\ (0.929) = 93\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 92.8\ (3.11) = 290\ \mu g/g$$

Coefficient of Repeatability = (289/400.5) x 100 = 72%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 274\ (0.929) = 250\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 254\ (3.06) = 780\ \mu g/g$$

Coefficient of Reproducibility = (777/400.5) x 100 = 190%

(continued)

* Sample identification (by letter) and analysis number.
† G3 measurement not performed.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) G2	G3	Calculations (G2-G3)	$\lvert(G2-G3)-(\overline{G2}-\overline{G3})\rvert$	(G2+G3)	$\lvert(G2+G3)-(\overline{G2}+\overline{G3})\rvert$
01	284	616	-332	272	900	214
02†	-	-	-	-	-	-
04	60	45	15	75	105	581
05	240	310	-70	10	550	136
06	450	520	-70	10	970	284
07	42	84	-42	18	126	560
08	574	840	-266	206	1414	728
09	294	140	154	214	434	252
10	372	383	-11	49	755	69
11	504	532	-28	32	1036	320
12	163	99	64	124	262	424
14	459	536	-77	17	995	309
Average	313	373		$X_1 = 93.4$		$X_2 = 355$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 93.4\ (0.929) = 87\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 96.8\ (3.11) = 270\ \mu g/g$$

Coefficient of Repeatability = (270/343) x 100 = 79%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 260\ (0.929) = 240\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 242\ (3.06) = 740\ \mu g/g$$

Coefficient of Reproducibility = (740/343) x 100 = 220%

(continued)

* Sample identification (by letter) and analysis number.
† G3 measurement not performed.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (µg/g) H1	H2	Calculations (H1-H2)	$\lvert(H1-H2)-(\overline{H1}-\overline{H2})\rvert$	(H1+H2)	$\lvert(H1+H2)-(\overline{H1}+\overline{H2})\rvert$
01†	-	-	-	-	-	-
02	350	334	16	69	684	59
04	576	233	343	258	809	66
05	290	260	30	55	550	193
06	280	140	140	55	420	323
07	182	154	28	57	336	407
08	573	489	84	1	1062	319
09	420	248	172	87	668	75
10	553	434	119	34	987	244
11	376	423	-47	132	799	56
12	522	273	249	164	795	52
14	432	629	-197	282	1061	318
Average	414	329		$X_1 = 108$		$X_2 = 192$

Standard Deviation for Repeatability:

$$S_1 = X_1K_1 = 108\ (0.929) = 100\ \mu g/g$$

Estimate of Repeatability:

$$R_1 = S_1K_2 = 100\ (3.11) = 310\ \mu g/g$$

Coefficient of Repeatability = (311/372) x 100 = 84%

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 156\ (0.929) = 140\ \mu g/g$$

Estimate of Reproducibility:

$$R_2 = S_2K_3 = 145\ (2.99) = 430\ \mu g/g$$

Coefficient of Reproducibility = (434/372) x 100 = 120%

(continued)

* Sample identification (by letter) and analysis number.
† Tube readings were off scale; no measurements were reported.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (μg/g) H1	H3	Calculations (H1-H3)	$\lvert(H1-H3)-(\overline{H1}-\overline{H3})\rvert$	(H1+H3)	$\lvert(H1+H3)-(\overline{H1}+\overline{H3})\rvert$
01†	-	-	-	-	-	-
02#	-	-	-	-	-	-
04	576	483	93	165	1059	75
05	290	170	120	192	460	524
06	280	4200	-	-	-	-
07#	-	-	-	-	-	-
08	573	375	198	270	948	36
09	420	517	-97	25	927	57
10#	-	-	-	-	-	-
11	376	495	-119	47	871	113
12	522	1060	-538	466	1582	598
14	432	601	-169	97	1033	49
Average**	456	528		X_1 = 180		X_2 = 207

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 180\ (0.954) = 170\ \mu g/g$**

Estimate of Repeatability:

$R_1 = S_1K_2 = 172\ (3.32) = 570\ \mu g/g$**

Coefficient of Repeatability = (571/492) x 100 = 120%**

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 194\ (0.954) = 180\ \mu g/g^{**}$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 185\ (3.04) = 560\ \mu g/g$**

Coefficient of Reproducibility = (562/492) x 100 = 110%**

(continued)

* Sample identification (by letter) and analysis number.
† Tube readings were off scale; no measurements were reported.
# H3 measurement not performed.
** Data pair from Lab No. 6 has been excluded because of outlier value.

TABLE D-1. (Continued)

Lab No.	Sample Analyses* (μg/g) H2	H3	Calculations (H2-H3)	$\lvert(H2-H3)-(\overline{H2}-\overline{H3})\rvert$	(H2+H3)	$\lvert(H2+H3)-(\overline{H2}+\overline{H3})\rvert$
01†	–	–	–	–	–	–
02#	–	–	–	–	–	–
04	233	483	-250	86	716	178
05	260	170	90	254	430	464
06	140	4200	–	–	–	–
07#	–	–	–	–	–	–
08	489	375	114	278	864	30
09	248	517	-269	105	765	129
10#	–	–	–	–	–	–
11	423	495	-72	92	918	24
12	273	1060	-787	623	1333	439
14	629	601	28	136	1230	336
Average**	365	529		$X_1 = 225$		$X_2 = 228$

Standard Deviation for Repeatability:

$S_1 = X_1K_1 = 225\ (0.954) = 220\ \mu g/g$**

Estimate of Repeatability:

$R_1 = S_1K_2 = 215\ (3.32) = 710\ \mu g/g$**

Coefficient of Repeatability = (714/447) x 100 = 160%**

Standard Deviation for Reproducibility:

$$S_2 = K_1\sqrt{(X_1^2+X_2^2)/2} = 226\ (0.954) = 220\ \mu g/g^{**}$$

Estimate of Reproducibility:

$R_2 = S_2K_3 = 216\ (3.04) = 660\ \mu g/g$**

Coefficient of Reproducibility = (657/447) x 100 = 150%**

* Sample identification (by letter) and analysis number.
† Tube readings were off scale; no measurements were reported.
\# H3 measurement not performed.
** Data pair from Lab No. 6 has been excluded because of outlier value.